A STUDY OF FORMALDEHYDE EXPOSURES FROM METALWORKING FLUID OPERATIONS USING HEXAHYDRO-1,3,5-TRIS (2-HYDROXYETHYL)-S-TRIAZINE

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EXECUTIVE SUMMARY

A large industry-wide study of formaldehyde exposures from metalworking fluid operations using Triazine biocides was undertaken by the Triazine Joint Venture. This study was in response to a recent OSHA regulation (CFR 1910.1048) covering employers and manufacturers which use and produce materials which may off-gas formaldehyde. Twelve operations at eight different facilities were evaluated for exposures to formaldehyde. The facilities surveyed included chemical blending, sheet metal rolling, general manufacturing, automotive manufacturing and aluminum can manufacturing.

Approximately 550 air samples were taken on workers and in areas where metalworking fluid containing Triazine was used. Air samples were taken in the morning, and were replaced in the afternoon after Triazine was freshly added to the metalworking fluid system. Short-term air samples were also taken during the addition of concentrated Triazine. Air samples were taken in areas of each facility where no Triazine was in use to evaluate the background levels of formaldehyde. In addition, field blank samples, samples spiked with formaldehyde and duplicate field samples were all taken to evaluate the ability of three different air sampling methods to monitor low levels of formaldehyde.

Employees using metalworking fluids containing Triazine at efficacious concentrations 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. Employees who added concentrated Triazine to metalworking fluid systems were never exposed to a measurable concentration of formaldehyde. Several air samples taken inside totally enclosed sumps with no mechanical exhaust ventilation exceeded the 0.5 ppm level. However, these were areas where employees did not enter during their normal work. The Triazine Joint Venture believes the data contained in this report can be used by employers, who use Triazine biocides in metalworking fluid systems, to avoid having to perform baseline exposure monitoring, as required by OSHA in the Formaldehyde Standard.

Air samples were taken at each location where no metalworking fluid was being used to determine background levels of formaldehyde. A number of these locations had detectable levels of formaldehyde. At two of the eight facilities, background levels were responsible for exposures measured above 0.1 ppm. Therefore, the results are expressed in this report both as uncorrected values (due to all sources of formaldehyde) and corrected so that exposures due predominantly to the use of Triazine could be determined.

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

personal exposures above 0.1 ppm. The same data corrected for background levels and spiked recoveries of formaldehyde showed that eight of the 12 operations had at least one personal sample above 0.1 ppm, and that eight of these operations had the majority of personal exposures below 0.1 ppm. Area air samples consistently resulted in lower formaldehyde values than for comparable personal air samples. When results were corrected for background and spiked recoveries, eight of the 12 operations had 90 percent or more of the area air samples below 0.1 ppm.

A statistical evaluation of the results of this study confirmed that there was a predictive relationship between Triazine levels in metalworking fluid and formaldehyde exposures. Regression analyses of the data indicated that levels of 250 ppm or less of Triazine were necessary to insure that no employee would be exposed to formaldehyde levels above 0.1 ppm. At the recommended dosage of Triazine in metalworking fluid (1000-1500 ppm), personal exposures would be expected to exceed 0.1 ppm of formaldehyde approximately 30-50 percent of the time.

Fifty of the nearly 550 air samples taken during this study were performed in duplicate to determine the precision of the different air sampling methods used to measure formaldehyde. When precision was calculated at the 95 percent confidence limit, variability of ±40-65% (depending on the sampling method) resulted. When the exposure data are considered using this information, a substantial portion of the data cannot be determined to be either above or below 0.1 ppm.

The OSHA Formaldehyde Standard requires employers to label products which may release formaldehyde at levels which could result in exposures above 0.1 ppm as an eight-hour time-weighted average. The standard also requires that when levels exceed 0.1 ppm, employers provide hazard communication training for their employees related specifically to the hazards of formaldehyde. OSHA has established certain precision and accuracy requirements for monitoring formaldehyde at the Permissible Exposure Limit of 0.75 ppm and Short Term Exposure Limit of 2.0 ppm. The data from this study suggest that current methods do not allow for precise formaldehyde monitoring at 0.1 ppm. It is anticipated that the data from this survey will be used to request an interpretation of this part of the regulation from OSHA.

The results from this study confirm that most metalworking fluid operations which use Triazine biocides will have some employee exposures above the 0.1 ppm level. Unless employers have their own exposure data indicating formaldehyde levels below 0.1 ppm, a conservative approach would suggest employers follow the requirements of the formaldehyde standard. These include modifying existing hazard communication training to incorporate information about possible formaldehyde exposure from metalworking fluids containing Triazine.

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INTRODUCTION

The formaldehyde study described in this report was sponsored by the Triazine Joint Venture (referred to as the Joint Venture throughout this report). This is a non-profit organization comprised of five major manufacturers of Triazine: Angus Chemical Company, Stepan Chemicals, Buckman Laboratories, L & F 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.

Triazine is the commercial name for Hexahydro-1,3,5-Tris(2-hydroxyethyl)-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.

The OSHA Formaldehyde Standard

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. This standard, like other OSHA health standards, has provisions for labelling, exposure monitoring, medical surveillance, training and engineering controls. Permissible Exposure Limits (PEL) were 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 (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 labelled 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.

Purpose of the Joint Venture's Formaldehyde Study

Members of the Joint Venture met in late 1992 to discuss the labelling requirements for their products. All manufacturers confirmed that their products contained well below 0.1% formaldehyde, which would not trigger labelling requirements. Limited laboratory and workplace data were shared among members. The members of the Joint Venture concluded that there were data which indicated the possibility that the use of Triazine could result in employee exposures above 0.1 ppm, but that there was no data suggesting exposures could exceed 0.5 ppm.

Members of the Joint Venture determined that their products were exempt of the labelling requirements, due to preemption by EPA FIFRA requirements which approve regulated biocide labels. They did release 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.

Development of a Study Protocol

Members of the Joint Venture discussed the various items which could influence the release of formaldehyde in the workplace. These included:

- The nature of the work and equipment used for machining.

- The concentration of Triazine in the metalworking fluid.

- The pH and temperature of the metalworking fluid.

- The size of the workplace.

- The ventilation which exists at a workplace.

- The level of bacterial contamination of the metalworking fluid.

Because of the existing regulatory requirements of the OSHA formaldehyde standard, members of the Joint Venture did not feel that a long-term (e.g. two to four year) study which addressed each issue raised above was in the best interests of either Triazine customers or manufacturers. A goal was established to initiate a study by August or September of 1993 and complete it by the end of the year. While the study might not answer all regulatory issues, it would minimally establish a comprehensive database which could be added to in the future by others.

A proposed protocol was presented in May at the 1993 annual meeting of the Society of Tribologists and Lubrication Engineers in Calgary, Canada. Suggestions for changes in the protocol were requested along with potential sites for conducting the study.

<u>Study Protocol</u>

The protocol used for this study consisted of the following:

(1) Site Selection

Every effort was made to evaluate Triazine exposures at a range of different manufacturing sites. Aluminum can manufacturers were selected for testing because they consistently maintain an efficacious concentration of Triazine 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. The concentration of Triazine 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.

(2) Methods of Exposure Monitoring

Monitoring was performed on employees machining using Triazine-containing metalworking fluid, in areas which represented locations where employees typically worked, and at sources (e.g. metalworking fluid sumps) where the highest concentrations of formaldehyde were expected. Background formaldehyde levels were also measured at areas not using Triazine-containing metalworking fluid. Formaldehyde monitoring was performed using three different methods all of which are described later in this section. Passive dosimeters and silica-gel tubes were used for personal, area and source monitoring. Impingers, which contain liquid solutions, were only used for area and source monitoring.

The sampling strategy consisted of monitoring the exposure of three to five employees in a specific area of a plant using 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 are samples handled in the normal manner (from the same manufacturers' lot, taken into the workplace, and submitted to a laboratory at the same time) but which had no air drawn through the sampling media. Some samples, both on employees and in areas, were performed 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) containing one microgram/microliter was taken into the field along with several micro-syringes. 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 formaldehyde was able to be accurately measured. Some field blanks were also spiked to determine if there was any difference caused by sampling air at the plant (positive or negative interferences).

(3) Other Data Collected

In addition to exposure data, samples of the metalworking fluid were obtained prior to and after the addition of Triazine. These were taken back to a laboratory and analyzed within three to seven days for pH and Triazine levels. Some notes were made as to the overall exhaust ventilation present at the facility. Photographs of various operations and employees were taken at many of the sites to document the type of operations employed.

(4) Issuing Reports

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 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.

SAMPLING AND ANALYTICAL METHODS

Monitoring formaldehyde

The measurement of formaldehyde levels in the atmosphere has been a dynamic area of industrial hygiene, with many new devices being developed to meet widespread interest in measuring formaldehyde in indoor environments (e.g. office buildings, mobile homes) along with traditional workplaces. Many manufacturers of these devices have struggled to meet the OSHA accuracy requirements at the 95% confidence limit of ±25% for monitoring at the PEL of 0.5 ppm and ±35% at the STEL of 2 ppm[(1)].

It was clear from the beginning of this study that a major difficulty would be accurately measuring formaldehyde levels at or below 0.1 ppm, the threshold level set by OSHA for labelling and training. We chose to use more than one method for monitoring formaldehyde due to the difficulties expected. A major study which compared a variety of active and passive sampling devices for formaldehyde by Noble et al. was published in late 1993[(2)]. Because of personal knowledge of the study, we had access to this information in early 1993 while planning this study.

NIOSH Method 3500

The first method considered was the NIOSH method 3500 which employs the use of midget impingers containing 0.1% sodium bisulfite solution. This is the traditional method for monitoring formaldehyde, and it is often a standard method for which new methods are compared. Formaldehyde is absorbed in the solution and forms sodium bisulfite-formaldehyde. This solution is brought back to a laboratory where it is reacted with chromotropic and sulfuric acids and measured using a visible absorption spectrometer.

This method was originally published by NIOSH in 1984 and updated in 1989. It is reported to have a range of 2-40 μg with a limit of detection of 0.5 μg. The method reports positive interferences from some oxidizable organic compounds, negative interferences from large excesses of phenol, alcohols and some aromatic hydrocarbons.

This method has been mostly evaluated at significantly higher concentrations of formaldehyde. Beasley et al. reported that over the range of 0.8-2.2 ppm of formaldehyde, sampling with this method resulted in approximately 25% lower levels than using DNPH-coated silica-gel tubes[(3)]. Noble et al. reported good precision with their testing of the NIOSH method 3500 with a coefficient of variation between 2.5-9% when tests were made for six hours at 0.3-0.5 ppm of formaldehyde[(2)].

A major drawback to this method is that it requires the presence of a liquid sampler which is not conducive to personal monitoring due to the possibility of spills. The purpose of selecting this method was primarily as a reference for the other two methods used in this study. This method recommends the use of two impingers in series. This would have doubled our analytical efforts to analyze these samples, and we did not expect breakthrough of formaldehyde from the first impinger due to the low levels expected. The study by Noble et. al failed to find any formaldehyde in a second impinger. Our own laboratory study, described later, also confirmed the lack of breakthrough of formaldehyde in the first impinger. Therefore, only one impinger was used in this study.

DNPH Passive Dosimeters

Passive dosimeters are sampling devices which require no mechanical air sampling pumps, are lightweight, simple to use, and particularly suitable for use by employees with minimal training in industrial hygiene. They also allow a large number of samples to be taken with minimal efforts. We determined that these were ideal devices to be tested and possibly recommended to small or medium-sized facilities using Triazine who would like to obtain formaldehyde exposure data.

There are a number of commercially available passive dosimeters for formaldehyde. The major problem with these devices are that they have an inherent low sampling rate which does not allow for monitoring low exposure levels of formaldehyde. The GMD 570 series passive dosimeter for formaldehyde was developed in collaboration with the National Institute of Occupational Health in Sweden[4,5]. It utilizes a pad impregnated with 2,4-dinitro phyenylhydrazine (DNPH). The method is based on the formation of a stable hydrazone (2,4-dinitrophynylhydrazone). The hydrazone is eluted with acetonitrile in a laboratory and analyzed by high-pressure liquid chromatography utilizing an ultraviolet detector. The manufacturer states that the device samples at 25.2 ml/min and has a lower limit of detection corresponding to 5 ppb for a full eight-hour shift. The dosimeter is somewhat unique in that the DNPH coated pad in the dosimeter is split in half. Only half of it is exposed to the air and the other half serves as a blank. Unfortunately, this results in performing two analyses for every single sample taken.

The GMD dosimeter was selected over a variety of other devices based on the study by Noble et al.[2]. They reported that the GMD dosimeter was the best performing passive dosimeter at the 0.5 ppm Action Level. Since the objectives of this study were to measure even lower levels, the high sampling rate and low detection limits made this a logical choice for this study.

DNPH Silica-Gel Tubes

EPA method TO-11 for formaldehyde is based on sampling using sorbent cartridges containing 2,4-dinitrophyenylhydrazine (DNPH) on silica gel. The chemistry of this method is similar to that described for the GMD dosimeter. SKC recently began selling small silica-gel tubes impregnated with DNPH, which could be used with small battery-operated pump for personal sampling.

Noble et al. tested DNPH tubes in their study, but they were forced to make their own tubes since these were not available at that time. They found that sampling with this method produced good precision but lower results than the NIOSH method 3500 at 0.3 and 0.5 ppm.

The advantage of this method is that it essentially uses the same chemistry as the GMD device, but allows a higher sampling rate. This in theory could enhance the sensitivity of the method when examining low levels of formaldehyde. In addition, the tubes could be adapted with a prefilter, unlike the passive dosimeters, to separate particulates from gaseous formaldehyde.

Analyses of Samples

All samples were analyzed by two laboratories which are accredited by the American Industrial Hygiene Association and participate 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, normally within 48 hours of sampling.

Analyses of Metalworking Fluids

Samples of metalworking fluids from each location were obtained before and after the addition of Triazine. These samples were brought back to an Olin analytical laboratory for analyses of both pH and Triazine levels. The pH was obtained using a standard electronic meter. Triazine levels were determined by derivitization with oxalyl dihydrazide. This forms a hydrazone which will produce a blue-colored complex when reacted with an excess of cupric ions. The reaction product is measured quantitatively with a visible spectrophotometer at 610 nm. The method is a modification of one described by Pesez and Bartos[6,7]. Most samples were analyzed for pH within three to five days of obtaining the sample.

The temperature of the metalworking fluid was noted where a facility provided measurement data. If the facility did not have measurement data, no measurements were recorded.

References

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(4) Levin, J., R. Lindahl and K. Andersson: High Performance Liquid Chromatographic Determination of Formaldehyde in Air in the PPB to PPM Range using Diffusive Sampling and Hydrazine Formation. National Institute of Occupational Health, Research Department in Umea, Sweden. Sweden Environmental Technical Letter 20 pp. 1423-1430 (1988).

(5) GMD Systems, Inc.: 570 Series Formaldehyde Dosimeter Badge: Instructions for Use and Sample Analyses. GMD Instructions, Issue #4 (1993).

6. Pesez and Bartos: Colorimetric and Fluorometric Analysis of Organic Compounds and Drugs. Clinical and Biochemical Analyses Series, Vol 1: Marcel Dekker, Inc., pp. 255-257 (1974)

7. Olin Corporation: Determination of Hexahydro-1,3,5-tris (2-hydroxyethyl)-s-triazine in Metalworking Fluids. Olin Corporation, Olin Biocides Application Data Sheet #735-051 (1990).

STATISTICAL HANDLING OF FORMALDEHYDE EXPOSURE DATA

Limits of Quantification for Formaldehyde Samplers

One of the challenges of this study was to attempt to accurately measure formaldehyde exposures at or below 100 ppb. Often limits of detection are used to determine how accurately one can measure a contaminant in air. Limits of detection would only consider the sensitivity of analytical equipment used for measuring formaldehyde. To determine the effect of formaldehyde contamination of samplers and the ability to detect low levels of formaldehyde due solely to its presence in the atmosphere, the limits of quantification were determined for each sampling method. These values reflect the lowest level where reliable results could be reported.

Field blank samples were taken at each of the eight locations visited during this study. A total of 22 blank impinger samples, 27 blank silica-gel tubes and 38 blank dosimeter samples were taken at these various locations. The results of all these field blank samples are shown by location in Table I. All 21 impinger samples were reported as non-detectable with a limit of detection of one microgram. A study performed in a laboratory setting, however, confirmed that this method could only reliably detect formaldehyde in quantities greater than five micrograms. Therefore, the limit of quantification for this method was set at 5 micrograms.

The results of 38 blank dosimeter samples brought back from the workplace is shown in Figure 1. The data do not graph well due to the fact that more than half the values were reported as non-detected, less than 40 nanograms of formaldehyde. A level of 200 nanograms was chosen as the approximate upper 95% value from these blanks.

The results of 27 blank silica-gel tube samples brought back from the workplace are displayed as a probability plot in Figure 2. It can be seen that the data are distributed in a linear manner as would be expected from random, non-systematic errors. We chose to use the upper 95% value of these data for our limit of quantification, resulting in a value of 550 nanograms of formaldehyde. Therefore, when formaldehyde values are reported in this study, these values are above levels due to contamination in our sampling media or analytical error.

The limits of quantification were only used for reporting less than values in this study. They were not used for subtracting actual measured values and reporting results (see subtracting blank samples). A comparison of limit of detection values and limit of quantification values is shown in Table II. Although the limit of quantification values are significantly higher than the limit of detection values, all three methods are capable of reporting values well below 100 ppb for a four-hour duration and well below the OSHA STEL value of 2000 ppb for a 15-minute exposure.

Subtracting Background Levels From Field Samples

It is conventional to subtract any contaminant from field blanks from each value obtained while performing exposure monitoring in the workplace. This is especially significant for formaldehyde and other substances which are ubiquitous in the environment. In the case of impingers, no subtraction was necessary since each field blank was determined to be non-detectable. For silica-gel tubes the average of all the field blanks from each location were used to subtract reported values.

GMD passive dosimeters are designed with a DNPH pad that is divided into two sections. Only half the pad is exposed to air, and the manufacturer states that the other half should be used as a blank value. Although this is a costly analytical approach for field blanks, due to problems discussed below we followed the manufacturer's instructions.

Problems With GMD Passive Dosimeters Noted In This Study

Each GMD passive dosimeter required a dual analyses: measurement of the exposed "A" side and the unexposed "B" side. It was decided to see if a pooled blank value could be used to save costs by reducing the number of analyses. This was determined to be impossible due to the large variability in levels reported in the "B" side of the dosimeter. At each location where the dosimeters were tested, there was usually at least a two-fold difference between the lowest reported "B" side value and the highest value reported.

Table III presents data from each test site by the concentration of formaldehyde measured and the levels detected on the two portions of each dosimeter. For all test locations, except #3, all dosimeters used were from the same manufacturer's lot. At test location #3, the background levels of formaldehyde on the unexposed side of the dosimeter were an order of magnitude higher than levels found at other sites.

It is not clear why the manufacturer could not produce a consistent level of formaldehyde for the adsorbent. Formaldehyde detected on the unexposed portion could not have resulted from breakthrough from the exposed side because: chemisorption of formaldehyde results in very tight chemical bonds which will not allow for migration in the adsorbent bed, and the levels measured in this study were far too low to overwhelm the capacity of the exposed side to adsorb formaldehyde. One possibility is that the dosimeter housings were not airtight and some formaldehyde was diffusing through cracks and leaks. If this were the case, there should be a positive relationship between the airborne concentration of formaldehyde detected and the background levels measured on the "B" side of the dosimeter. When this theory is tested, there is no clear result. The data from Site #4 was found to have a strong positive correlation with a coefficient of correlation of 0.57, which was statistically significant at $p < 0.03$. The data from Site #5 was also found to have a positive correlation which was not statistically significant.

For all sites except #3, variability in the dosimeters background level could vary by approximately 0.2-0.3 micrograms. This could result in reported differences as much as +/- 40 ppb. Clearly this effect would be much smaller if the housing leaked at an equal rate. Discussions with Janet Noble of Monsanto who conducted extensive testing on these dosimeters confirmed that dosimeters exposed to higher concentrations did have higher backgrounds. However, when these levels were subtracted, the dosimeters behaved in a precise manner. There does not appear to be any reason for discarding the data obtained in this study with these dosimeters, but these devices would not be recommended for future studies due to this problem.

TABLE I
RESULTS OF FIELD BLANKS BY LOCATION
(in nanograms-Formaldehyde)

Site #	Impingers	Silica-Gel Tubes	Dosimeters
1	<1000, <1000	447, 468	<40, 105
2	<1000, <1000, <1000	256, 249	89, 40
3	<1000, <1000	505, 607	<40, <40, <40 <40, 91
4	<1000, <1000	252, 260	238,181,236, 318,<40,<40
5	<1000, <1000	152, 160	275
6	<1000, <1000, <1000, <1000 <1000	230,235,204 212,163,152	71,<40,<40,<40 <40
7	<1000, <1000 <1000, <1000	294,374,217 247,141'	68,<40,85,<40 <40,<40,<40,<40 <40,<40
8	<1000, <1000	<40,49,99,105 225,315	<40,<40,<40,<40 <40,40, 60

TABLE II
COMPARISON OF LOD AND LOQ VALUES FOR ALL THREE SAMPLING METHODS

Sampling Device	Flow Rate (l/min)	Sample Time (min)	LOD (ppb)	LOQ (ppb)
Impinger	1.0	240	3	17
Impinger	1.0	15	54	270
Silica-Gel Tube	0.1	240	1	18
Silica-Gel Tube	0.1	15	22	297
GMD Dosimeter	0.0252	240	5	27
GMD Dosimeter	0.0252	15	85	426

TABLE III
EFFECT OF FORMALDEHYDE CONCENTRATION ON GMD BLANKS

	PPB Reported	μg-"A" Side	μg-"B" Side
Site #1			
	62	0.931	0.448
	210	0.724	0.366
	130	0.685	0.374
	< 99	0.363	0.362
	< 111	0.470	0.482
	< 39	0.555	0.426
	< 31	0.463	0.335
	< 26	0.470	0.399
	28	0.590	0.358
	< 63	0.505	0.400
Site #2			
	< 30	0.324	0.208
	< 21	0.177	0.107
	< 28	0.320	0.409
	< 30	0.359	0.482
	< 30	0.437	0.273
	< 31	0.361	0.293
	< 32	0.338	0.179
	< 31	0.340	0.388
	< 35	0.453	0.341
	< 31	0.379	0.339
	< 35	0.305	0.159
	< 35	0.425	0.385
	<1250	0.354	0.397
	< 540	0.301	0.130
	< 30	0.366	0.225
	< 30	0.490	0.400
	Blank	0.156	0.157
	Blank	0.264	0.169
	Blank	0.140	0.152
Site #3			
	< 55	0.683	0.665
	< 37	0.795	0.927
	< 56	0.907	0.886
	< 28	0.845	0.725
	< 41	0.795	0.872
	< 44	0.682	0.642
	< 39	0.853	1.13
	< 39	0.761	0.757
	<470	0.892	0.722
	< 60	1.27	1.08
	< 45	0.987	1.24

< 57	0.729	0.689
71	0.319	0.302
180	0.874	0.244
< 48	0.349	0.266
< 56	0.623	0.583
< 47	0.635	0.630
< 56	0.742	0.702
< 18	0.888	0.758
<360	0.806	0.854
470	5.77	2.67
160	4.07	3.36
250	4.86	3.26
410	4.72	2.82
160	4.19	3.26
140	3.96	3.30
320	3.78	1.88
270	4.29	3.09
340	5.18	3.58
180	6.09	4.99
< 44	4.48	4.08
270	4.81	3.21
< 33	3.27	2.87
60	4.77	2.87
72	6.19	3.89
62	2.52	2.09
230	3.39	2.39
Blank	0.588	0.610
Blank	0.535	0.567
Blank	0.804	0.898
Blank	0.725	0.634

Site #4

52	0.669	0.283
106	0.810	0.278
154	0.945	0.304
83	0.858	0.323
< 32	0.403	0.280
72	0.771	0.309
79	0.881	0.315
100	0.881	0.397
61	0.794	0.427
< 33	0.533	0.367
67	0.782	0.389
70	0.835	0.428
479	3.60	0.410
682	4.94	0.540
38	0.982	0.472
18	0.575	0.303
<463	0.417	0.579
Blank	0.524	0.500
Blank	0.501	0.467

Site #5

93	0.995	0.361
97	0.989	0.334
105	1.05	0.338
114	1.19	0.436
107	1.08	0.372
147	1.34	0.382
55	1.05	0.715
97	0.903	0.406
149	1.15	0.357
153	1.22	0.288
141	1.21	0.353
185	1.46	0.330
149	1.19	0.290
123	0.986	0.256
119	1.03	0.330
85	0.863	0.314
79	0.957	0.454
707	4.02	0.370
890	8.01	0.560
108	1.88	0.310
48	1.07	0.393
Blank	0.792	0.517
Blank	0.263	0.146
Blank	0.179	0.189
Blank	0.234	0.287
Blank	0.241	0.238

Site #6

<27	0.252	0.140
71	0.545	0.172
<27	0.258	0.155
410	2.41	0.220
< 27	0.260	0.182
140	0.669	0.202
< 30	0.286	0.175
< 30	0.267	0.201
< 62	0.423	0.225
160	0.711	0.184
< 33	0.231	0.160
320	1.90	0.220
< 33	0.260	0.230
64	0.560	0.223
< 34	0.251	0.286
< 34	0.282	0.227
130	0.960	0.287
140	0.997	0.248
130	0.869	0.207
< 30	0.394	0.264
43	0.453	0.221

< 30	0.385	0.204
< 32	0.458	0.248
45	0.489	0.240
56	0.516	0.210
36	0.424	0.200
< 38	0.353	0.263
39	0.506	0.270
150	1.03	0.270
< 33	0.452	0.276
< 33	0.418	0.274
41	0.570	0.333
54	0.500	0.186
180	1.35	0.230
30	0.582	0.177
22	0.516	0.223
< 15	0.262	0.279
< 16	0.359	0.271
<238	0.295	0.197
<238	0.210	0.200
<238	0.226	0.207
Blank	0.312	0.241
Blank	0.219	0.240
Blank	0.290	0.280
Blank	0.187	0.166
Blank	0.196	0.172

Site #7

150	1.11	0.129
115	1.16	0.174
127	0.895	0.123
131	1.19	0.114
127	0.958	0.143
108	0.104	0.128
121	0.860	0.129
143	1.01	0.144
96	0.986	0.191
123	1.209	0.202
78	0.567	0.101
73	0.641	0.206
83	0.867	0.107
67	0.766	0.152
208	1.37	0.117
58	0.629	0.888
294	1.90	0.153
360	3.42	0.157
<726	0.109	0.122
<726	0.210	0.132
139	0.992	0.150
126	1.23	0.118
133	0.968	0.121
135	0.950	0.087

123	1.13	0.111
118	1.16	0.185
101	0.811	0.187
131	0.958	0.155
80	0.891	0.200
89	0.959	0.191
114	2.04	0.250
111	1.95	0.215
158	2.61	0.233
Blank	0.262	0.194
Blank	0.217	0.187
Blank	0.264	0.179
Blank	0.167	0.221
Blank	0.156	0.148
Blank	0.174	0.193
Blank	0.197	0.180
Blank	0.087	0.091
Blank	0.083	0.098
Blank	0.091	0.087

Site #8

98	1.66	0.255
122	1.88	0.223
147	2.35	0.268
134	2.00	0.233
148	2.20	0.264
65	1.21	0.335
74	1.21	0.214
66	1.08	0.214
42	0.762	0.215
43	0.750	0.201
40	0.722	0.207
126	1.69	0.210
162	2.13	0.228
135	1.92	0.241
154	2.06	0.264
35	0.592	0.190
34	0.566	0.181
Blank	0.228	0.230
Blank	0.218	0.214
Blank	0.184	0.179
Blank	0.265	0.270
Blank	0.241	0.198
Blank	0.230	0.204
Blank	0.278	0.214
Blank	0.221	0.195
Blank	0.222	0.236

FIGURE 1

PROBABILITY PLOT OF BLANK VALUES

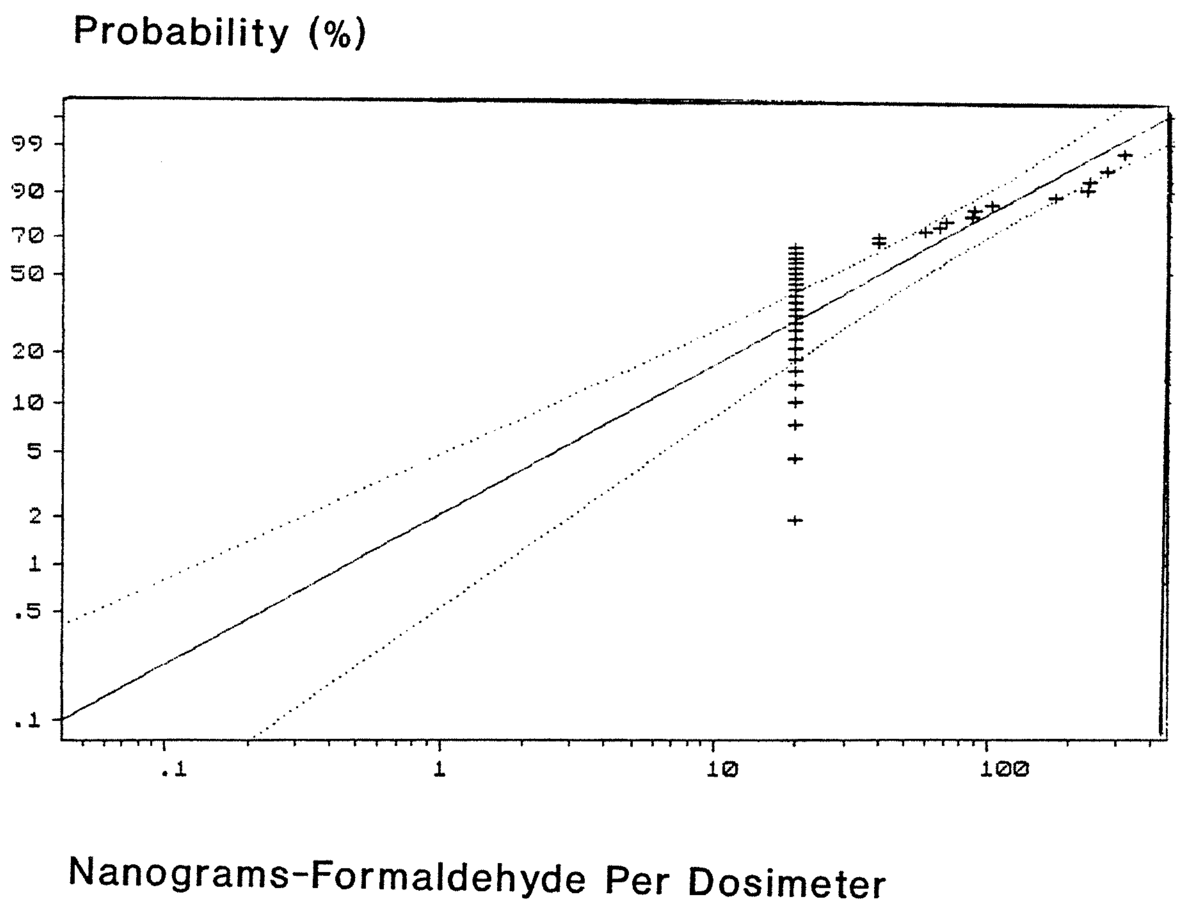
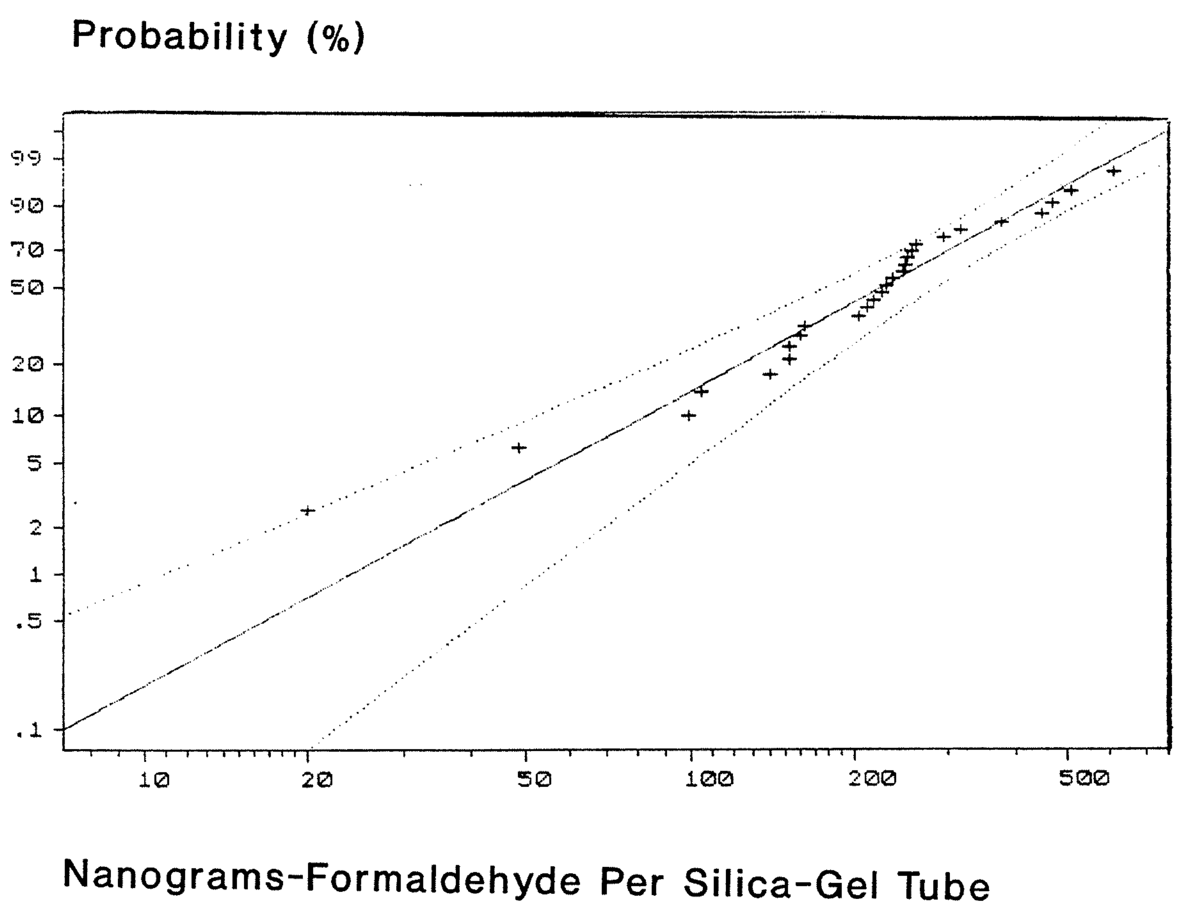


FIGURE 2

PROBABILITY PLOT OF BLANK VALUES



INITIAL LABORATORY TESTING

Introduction

Laboratory studies were performed to evaluate the three sampling methods and their ability to recover known quantities of formaldehyde. A solution of 37% formaldehyde in water (10% methanol added for stabilization) was diluted 1:1000 and 5 and 10 μl aliquots (1.85 and 3.7 μg of formaldehyde, respectively) were added to the three different sampling media chosen for the study: 1% sodium bisulfite solution, DNPH treated silica-gel tubes and a passive dosimeter utilizing a filter impregnated with DNPH. This was accomplished using a micro-syringe and formaldehyde was injected directly into the media. Samplers were placed in a laboratory setting with no known sources of formaldehyde and allowed to sample for approximately five to six hours. Most of these samplers were spiked in triplicate and they were placed next to unspiked samplers.

A second series of tests were undertaken to determine whether a 37 mm mixed-cellulose filter, placed in front of either the silica-gel tube or impinger would interfere with the collection of formaldehyde gas. It was thought that the presence of an aerosol of metalworking fluid containing Triazine might create a positive interference with the sampling methods. Only the two active sampling methods, silica-gel tubes and impingers, could accommodate the addition of a filter. Filters were spiked with 1.85 and 3.7 μg of formaldehyde as discussed above and then attached to silica-gel tubes and impingers. These devices were operated for approximately five to six hours and compared to samples where no spikes were made.

A third series of tests were made to determine if Triazine would result in a positive interference with the different sampling devices. Several assumptions were made when designing this experiment. It was assumed that a very high aerosol concentration of 10 mg/m^3 of metalworking fluid could be present in the workplace (as an eight-hour time-weighted average), and that this aerosol would contain 1500 ppm of Triazine. Based on this assumption and estimated flow rates of 1 l/min for impingers, 0.1 l/min for silica-gel tubes and 0.0252 l/min for dosimeters; these devices were spiked with the equivalent of 11.52 μg, 0.72 μg and 0.18 μg of concentrated Triazine. This was accomplished by taking a standard stock Triazine solution, diluting it 1:10,000 with water. The following aliquots were spiked in the sampling media: 115 μl for impingers, 7 μl for silica-gel tubes and 2 μl for dosimeters. If all the formaldehyde bound in Triazine was released and measured as formaldehyde, this would be the equivalent of approximately four ppb of formaldehyde. Samples were spiked in duplicate or triplicate and allowed to sample laboratory air for six to seven hours, and compared to devices which were not spiked with Triazine.

This was repeated at a later date with only impingers in which an impinger containing 1% sodium bisulfite was placed in front of the spiked impinger to capture any residual formaldehyde in the atmosphere.

Results

The background level of formaldehyde in the laboratory was determined by the first series of experiments. The average formaldehyde concentration when nothing was added to the sampling media was used in subtracting background levels. The background for impinger sampling was 8.5 ppb, 16 ppb for silica-gel tubes and 18.5 ppb for dosimeters.

Mean values and relative standard deviations (standard deviation divided by the mean value) are presented in Table I. For most of the data, silica-gel tubes and dosimeters showed good precision with relative standard deviations below 10%. Data from impingers showed more variability, with relative standard deviations ranging from 12-24%.

More than 100 percent of the amount of formaldehyde spiked onto dosimeters and silica-gel tubes was recovered. When a filter was placed before silica-gel tubes and spiked with formaldehyde, the recovered values were 70-75% of the amounts which were recovered when no filter was used. This suggests that it was impossible to recover all the formaldehyde on a filter, and that the use of a pre-filter might result in erroneous lower values. Data with filters and impingers were too varied to make any meaningful assessment.

Data obtained when samplers were spiked with Triazine show a great deal of variability, owing to the very low levels which were spiked. It does appear that Triazine may be a positive interference in the analyses of formaldehyde, but that less than all of the potential formaldehyde bound in Triazine will be measured by any of the three samplers as free formaldehyde.

Blank media samples were submitted to each laboratory for analyses (samples which were handled normally, but which were not exposed to any air). Three impinger samples were all reported as non-detected, less than one microgram of formaldehyde. Two silica-gel tubes were reported as 0.45 and 0.47 μg of formaldehyde. Two dosimeters were reported as non-detected (<0.04 μg) and 0.11 μg of formaldehyde. Data in Table I are shown corrected for the average of the blank values, except dosimeters which were corrected for each blank sample as previously discussed.

Discussion

The amounts of formaldehyde spiked onto each type of sampler was thought to be sufficient to be above the detection limits of the method. The detection limits of the three methods were reported by the laboratories to be: 1.0 μg for impingers and 0.04 μg for both silica-gel tubes and dosimeters. The ability to recover formaldehyde is both a function of the detection limit and typical range of blank values. If formaldehyde levels are less than the average blank value plus or minus two standard deviations, a relative standard deviation of greater than five percent would be expected simply from the influence of the blank (note: other likely variables include air sampling pump fluctuations and analytical instrumentation and preparation variability). The spiked samples of 1.85 and 3.7 μg of formaldehyde for dosimeters and silica-gel tubes were sufficiently greater than the blank values and limit of detection to result in good precision. The spikes of Triazine had too little formaldehyde available to be sufficiently above the blank values. This may be the reason for the high variability with these results.

Although the limit of detection for impingers was reported as 1.0 μg, subsequent testing showed the value to be dependent on the quantity of liquid in the impinger. In general, a more realistic limit of detection of 5.0 μg appears appropriate. Given this, it is unlikely the impingers could have accurately recovered the small formaldehyde spikes which were placed in the media. This explains the variability with this method and the unreliable recoveries of low levels of formaldehyde.

The addition of Triazine in each sampler was based on a maximum expected concentration in the workplace and was adjusted for each type of sampler based on its flow rate. These tests with formaldehyde were done with just two different quantities regardless of the flow rates used by each device. This resulted in reasonable levels for detection in silica-gel tubes and dosimeters, but too low a level for dosimeters. As a result of this work, it was determined for field experiments to provide formaldehyde spikes realistic of what we would expect to find. We chose to use a level of 0.1 ppm (0.12 mg/m^3) of formaldehyde in the workplace and a sampling time of 240 minutes (four hours or approximately one-half an eight-hour workshift). Based on these assumptions, appropriate spiked quantities of formaldehyde would be: 30 μg for impingers, 3.0 μg for silica-gel tubes and 0.7 μg for dosimeters.

Another finding from this study was the confirmation that low background levels of formaldehyde were likely to be encountered in this study. The levels of 10-20 ppb (10-20% of the level of interest) was found in a laboratory with very few furnishings. Locations with particle board, panelling, and rugs would be expected to provide higher levels. Therefore, it was determined to monitor background levels of formaldehyde in all our field studies.

Finally, to the best of our knowledge no one had ever attempted to provide liquid spikes of formaldehyde to passive dosimeters. There was some question whether a dosimeter, which samples by passive diffusion, would be able to quantitatively capture most of this spike. The results of these experiments suggested that dosimeters could be successfully spiked with small quantities of formaldehyde solution.

TABLE I
RESULTS OF LABORATORY TESTING

Sample Type	Formaldehyde Results (ppb)	Less Background (μg)	% Recovery
Media Sampled for 5-6 Hours With Nothing Added			
Impinger	9		
Impinger with filter	8		
Silica-Gel Tube	17		
Silica-Gel Tube w/filter	15		
Dosimeter	20		
Dosimeter	17		
Media Sampled for 6-7 Hours With 1.85 μg Formaldehyde Spike			
Impinger	10	1.2	65
Impinger	15	4.7	250
Impinger	9	0.3	16
Mean:	**11**		
RSD:	**24%**		
(note: background level was equivalent to 6.7 μg spike)			
Silica-Gel Tube	52	1.8	97
Silica-Gel Tube	58	2.0	108
Silica-Gel Tube	61	2.1	114
Mean:	**57**		**106**
RSD:	**6.6**		
(note: background level was equivalent to a 0.8 μg spike)			
Dosimeter	220	2.3	124
Dosimeter	190	2.1	114
Dosimeter	220	2.3	124
Mean:	**210**		**121**
RSD:	**6.7**		
(note: background level was equivalent to a 0.2 μg spike)			
Media Sampled for 6-7 Hours With 3.7 μg Formaldehyde Spike			
Impinger	19	7.8	212
Impinger	15	4.9	132
Impinger	11	1.7	46
Mean:	**15**		
RSD:	**22%**		
(note: background level was equivalent to 6.6 μg spike)			
Silica-Gel Tube	110	4.6	124
Silica-Gel Tube	130	5.3	143
Mean:	**120**		**134**
(note: background level was equivalent to a 0.8 μg spike)			

TABLE I (Continued)
RESULTS OF LABORATORY TESTING

Sample Type	Formaldehyde Results (ppb)	Less Background (µg)	% Recovery
Media Sampled for 6-7 Hours With 3.7 µg Formaldehyde Spike			
Dosimeter	400	4.5	122
Dosimeter	420	4.6	124
Dosimeter	410	4.7	127
Mean:	**410**		**124**
RSD:	**2.0**		
(note: background level was equivalent to a 0.2 µg spike)			
Media Sampled for 4-5 Hours: 1.85 µg Formaldehyde Spiked On MCE Filter			
Impinger w/filter	8	<0.1	0
Impinger w/filter	16	4.1	222
Mean:	**12**		
(note: background level is equivalent to a 5.1 µg spike)			
Silica-Gel Tube w/filter	60	1.5	81
Silica-Gel Tube w/filter	58	1.4	76
Mean:	**13**		**79**
(note: background level is equivalent to a 0.5 µg spike)			
Media Sampled for 4-5 Hours: 3.7 µg Formaldehyde Spiked On MCE Filter			
Impinger w/filter	16	4.1	111
Impinger w/filter	9	<0.1	0
Mean:	**13**		
(note: background level is equivalent to a 5.1 µg spike)			
Silica-Gel Tube w/filter	119	3.4	92
Silica-Gel Tube w/filter	130	3.8	102
Silica-Gel Tube w/filter	124	3.5	95
Mean:	**124**		**96**
RSD:	**3.6**		
(note: background level is equivalent to a 0.5 µg spike)			
Media Sampled for 6-7 Hours With Spiked Quantities of Triazine			
Impinger	12	2.2	58
Impinger	9	<0.1	0
Impinger	10	0.3	8
Mean	**10**		
RSD	**12**		

(note 115 µl spike of a 1:10000 dilution of Triazine, equal to a maximum formaldehyde spike of 3.8 µg. Background level was equivalent to a 6.5 µg formaldehyde).

TABLE I (Continued)
RESULTS OF LABORATORY TESTING

Sample Type	Formaldehyde Results (ppb)	Less Background (μg)	% Recovery
Media Sampled for 6-7 Hours With Spiked Quantities of Triazine			
Silica-Gel Tube	12	<0.1	0
Silica-Gel Tube w/filter	18	0.2	100
Mean:	**15**		

(note 7 μl spike of a 1:10000 dilution of Triazine, equal to a maximum formaldehyde spike of 0.2 μg. Background level was equivalent to 0.8 μg formaldehyde).

Sample Type	Formaldehyde Results (ppb)	Less Background (μg)	% Recovery
Dosimeter	23	0.05	83
Dosimeter	21	0.02	33
Dosimeter	23	0.05	83
Mean:	**22**		
RSD:	**4.2**		

(note 2 μl spike of a 1:10000 dilution of Triazine, equal to a maximum formaldehyde spike of 0.06 μg. Background level was equivalent to 0.22 μg formaldehyde).

Media Spiked with Triazine (Equivalent of 3.8 μg Formaldehyde), But With No Airflow.

Sample Type	Formaldehyde Results (ppb)	Less Background (μg)	% Recovery
Impinger		<1.0	0
Impinger		<1.0	0
Impinger		<1.0	0

(there was no background of formaldehyde for these tests)

ADDITIONAL LABORATORY STUDIES

During the field portion of this study, there appeared to be a trend that facilities which had higher Triazine levels in their metalworking fluids had higher formaldehyde levels measured in their workplace. To test this hypothesis, a study was made in which the space above metalworking fluid containing various amounts of Triazine was tested for formaldehyde. Olin metalworking researchers provided 100 ml samples of semi-synthetic fluid containing 0-2000 ppm of Triazine. The pH of the solutions varied from 8.7-9.1. Fifty ml aliquots were put in a 125-ml Erlenmeyer flask, which was placed on a magnetic stirrer. Air was sampled from the top of the flask into an impinger containing 0.1 % sodium bisulfite. A second impinger was placed immediately after the first impinger. The purpose was to determine whether formaldehyde was effectively captured using a single impinger. Sampling was conducted for 60 minutes at 1 l/min.

A second series of tests were conducted to estimate the actual limit of detection for the NIOSH 3500 method. The method reports that the limit is 1 μg per sample. However, it appeared that this limit was dependent on the actual volume of fluid tested. For these tests, 20 mls of 0.1% sodium bisulfite were placed in a sample container and spiked with various aliquots of a 1 μg/μl formaldehyde solution.

Results

The results of these tests are shown in Tables I and II. The schematic of the headspace testing and results are also shown in Figures 1 and 2. The results of headspace testing confirm that there is a relationship between formaldehyde measured above metalworking fluid solution and the concentration of Triazine in solution. The results of repeat sampling indicated substantial variability with this protocol. It is not clear why there was this much variability. Seven of the nine impingers placed behind the first impinger failed to detect any formaldehyde. In two cases, trace levels (approximately 1% of the total amount) of formaldehyde were seen in the second impinger.

The results of low-level additions of formaldehyde to impinger solutions confirmed our suspicion that this method could not reliably detect down to 1.0 μg of formaldehyde. The method appears to be reliable at 5.0 μg of formaldehyde or greater.

Conclusions

These tests indicate that formaldehyde levels measured above metalworking fluid solutions are related to the concentration of Triazine in solution. There was not enough data to better define this relationship mathematically, and it appeared some refinements to the method are needed to improve the precision of replicate sampling.

The NIOSH 3500 method for formaldehyde calls for the use of a second impinger downstream from the original impinger to collect any excess formaldehyde. These results indicate that for the range of formaldehyde of interest in this study, these impingers are not needed and would simply serve to increase the analytical cost of the study.

The limit of detection of 1.0 μg reported in the NIOSH 3500 method was not substantiated by this study. Results suggest that a limit of 5.0 μg is more realistic for this study and this value was used for all field study results where no formaldehyde was detected.

TABLE I

RESULTS OF LABORATORY HEADSPACE TESTING OF METALWORKING FLUID

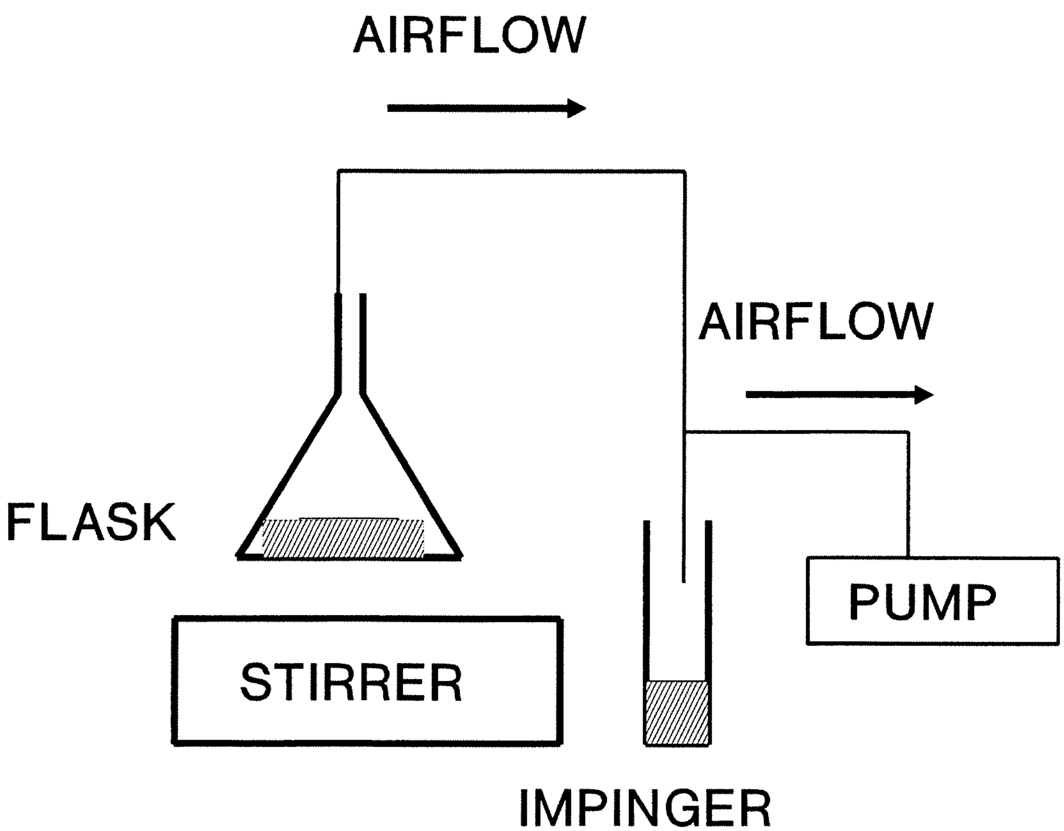
Concentration of Triazine	Formaldehyde Conc. (ppm) First Impinger	Second Impinger
0	< 0.01	< 0.01
250	0.32	< 0.01
250	0.47	< 0.01
500	0.63	< 0.01
500	1.13	0.01
1000	0.88	< 0.01
1000	2.47	0.02
2000	1.68	< 0.01
2000	1.85	< 0.01

TABLE II

RESULTS OF LOW-LEVEL FORMALDEHYDE SPIKES IN IMPINGER SOLUTION

Formaldehyde Added (μg)	Formaldehyde Detected (μg)	% Recovery
0	< 1.0	--
0	< 1.0	--
1.0	< 1.0	0
1.0	< 1.0	0
3.0	4.4	133
3.0	< 1.0	0
5.0	6.5	130
5.0	7.0	140
33.	38.7	117
33.	33.7	102

FIGURE 1
SCHEMATIC OF HEADSPACE STUDY

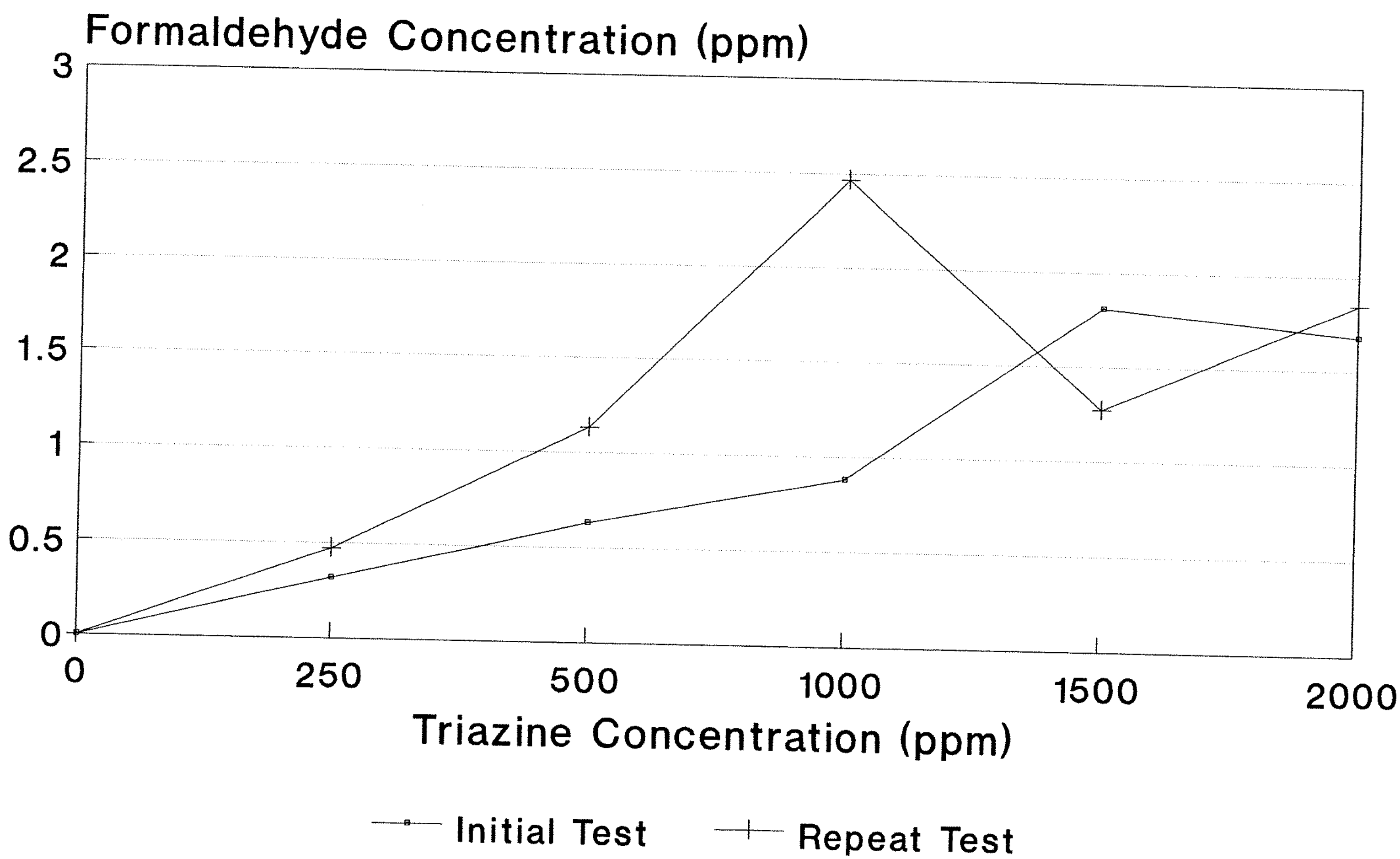


50 mls SEMI-SYNTHETIC FLUID (1:20)

pH 8.7-9.1

0-2000 PPM TRIAZINE (6)

FIGURE 2
LABORATORY HEADSPACE STUDIES



SITE #1

Summary

Operations at a specialty chemical facility blending concentrated Triazine solutions were evaluated. A total of 30 air samples, six personal and 24 area samples, were taken. Seventeen of the air samples were below the LOD, and four samples were above 100 ppb. None of the samples were above the OSHA Action Level of 500 ppb.

Background

The first site visited in this study was a medium-sized specialty chemical facility involved in blending several formulations of Triazine. Concentrated Triazine came into the facility in 55 gallon drums. These were slowly charged into a reactor by use of a vacuum hose. Empty drums were washed with water, and the effluent went into the facility's waste treatment facility. Several additives (non-formaldehyde releasing) were charged in the reactor and combined with Triazine, and then the product was gravity fed back into 55 gallon drums.

Chemical operators involved in these operations did many other non-related functions simultaneously. For example, if it took 30 minutes to charge a drum of Triazine into the reactor, the operator began the task and then performed various other jobs in different parts of the plant until he or she had to return to start the next drum. Because of this, we chose to emphasize area and source samples rather than personal samples. Many of these area samples probably did not represent normal exposure, and were closer to liquid Triazine than employees normally would work.

Results

The results of all monitoring are shown in Tables I and II. There were no efforts at this location to obtain background formaldehyde levels and there was only a few spiked samples taken in the field. The field spikes at this location were all at the same level of formaldehyde regardless of the device and its sampling rate. Subsequent site locations had spiked samples adjusted for the flow rate of the device, to coincide with a concentration of 100 ppb for a four hour sample.

A total of 30 air samples were taken during this survey; six were personal samples and 24 were area air samples. Only one of the six personal air samples was above 100 ppb, and a duplicate to this sample indicated a lower exposure below the limits of quantification (LOQ). Only four of the 24 area air samples were above 100 ppb. The majority of all air samples (17/30) were below the LOQ. None of the air samples approached the 500 ppb Action Level set by OSHA. The only operation which appeared to release measurable levels of formaldehyde was washing empty drums which contained Triazine.

Table I shows values corrected based on the average recoveries noted in Table II for each of the three methods. Please note that no corrections are made for devices which are reported to be below the LOQ. The dosimeter recoveries were unusually low, probably due to the large quantity of liquid formaldehyde which had to be spiked onto the dosimeter. This potential problem was corrected in future studies, when lower spiked values of formaldehyde were used.

TABLE I
RESULTS OF FORMALDEHYDE MONITORING AT SITE #1

SAMPLE TYPE	OPERATION	DURATION (min)	FORMALDEHYDE CONCENTRATION (PPB) REPORTED VALUE	CORRECTED VALUE
Personal Air Samples				
Tube	Charging Reactor	80	< 55	
Dosimeter	(duplicate sample)	80	130	203
Tube	Drumming Triazine	264	< 17	
Dosimeter	(duplicate sample)	264	28	44
Tube	Drumming Triazine	102	< 46	
Dosimeter	(duplicate sample)	102	< 63	
Area Air Samples				
Impinger	Over Drum Being Charged	251	< 10	
Tube	(duplicate sample)	251	34	27
Dosimeter	(duplicate sample)	251	62	99
Impinger	Over Drum Being Washed	54	80	88
Tube	(duplicate sample)	54	240	189
Dosimeter	(duplicate sample)	54	210	328
Tube	At Drum Weigh Station	235	< 19	
Dosimeter	(duplicate sample)	235	< 26	
Tube	At Drum Weigh Station	165	< 28	
Dosimeter	(duplicate sample)	165	< 39	
Tube	At Drum Weigh Station	165	< 20	
Dosimeter	(duplicate sample)	165	< 31	
Source Air Samples				
Impinger	On top of Triazine Drum, next to open bung-hole	65	< 39	
Tube	(duplicate sample)	65	< 70	
Dosimeter	(duplicate sample)	65	< 99	
Impinger	On top of Triazine Drum, next to open bung-hole	58	< 44	
Tube	(duplicate sample)	58	< 76	
Dosimeter	(duplicate sample)	58	< 111	

TABLE II
RESULTS OF FORMALDEHYDE MONITORING AT SITE #1
FIELD RECOVERIES OF FORMALDEHYDE SPIKES

Sample Type	Area/Personal	Spike(μg)	Recovery (μg)	%Recovery
AREA A				
Impinger	A	18.5	16.9	91
Impinger	A	37.0	33.6	91
Average recovery= 91%				
Tube	A	18.5	23.8	129
Tube	A	37.0	46.4	125
Average recovery = 127%				
Dosimeter	A	18.5	10.8	58
Dosimeter	A	37.0	25.4	69
Average recovery = 64%				

SITE #2

Summary

Two different metalworking operations were examined at a steel rolling mill. Each operation had its own central sump which supplied coolant to the rolling mills. The two operations were housed in the same building, several hundred yards apart.

A total of 59 air samples for formaldehyde were taken on employees and in areas related to these two operations. All six personal samples taken at one of the two mills indicated exposures to be below the LOQ. Five of the six personal samples taken at the other mill were either below the LOQ or less than 100 ppb. Only one sample, from an operator in Mill B, out of the 59 air samples taken, indicated an exposure above 100 ppb. This one sample was 110 ppb uncorrected, and 96 ppb corrected.

The mill with the highest reported levels of Triazine had the lowest exposure data. It is not clear why this occurred, except that exposures at Mill B increased with the addition of Triazine. Area and source air samples were low at both mills. None of the samples taken during the addition of Triazine indicated any measurable level of formaldehyde. All control samples taken at the plant were below the LOQ.

Background

The second site visited in this study was a steel rolling mill. Employees were monitored who worked at two different large steel rolling mills. Mill "A" employed two helpers and an operator. The operator tended to work at a central control area, while the two helpers loaded and unloaded steel rolls. The helpers worked closer to the machinery and could have received higher exposures. Mill "B" was a similar type of rolling mill only larger. This mill employed two helpers and two operators.

Each mill had its own metalworking fluid system. Mill A had a sump which contained 7,000 gallons of water-soluble metalworking fluid, located several hundred yards away. Mill B had a 15,000 gallon sump which was above ground and adjacent to the rolling mill. During the study, five gallons of concentrated Triazine was manually poured directly into the sump of Mill A and ten gallons to the sump of Mill B.

Both operations were housed in a large steel building which had exhaust fans located at the ends of the building. There was no local exhaust ventilation for any of these operations. Samples were taken in the morning, prior to the addition of Triazine, and repeated in the afternoon after Triazine was added.

Results

The results of all monitoring are shown in Tables I-IV. The results of monitoring the metalworking coolant are shown in Table V. All background samples were below the limits of quantification (LOQ) for the methods used, and no correction of the data for background levels of formaldehyde were made.

The results of recoveries of known levels of formaldehyde in field spikes are shown in Table IV. The data for Table I and II are shown both as reported values and corrected for spiked recoveries. All spiked recoveries were greater than 100%, so the corrected exposure data were reduced accordingly. There were few spiked samples taken for impingers and dosimeters, so the values from both mills were combined for correcting the values in Tables I and II. This study included a series of blank samples which were spiked with formaldehyde. These resulted in fairly similar values to those obtained in the field, with the exception of the dosimeters which were lower in the field. It is not clear what the sources of positive interferences are, except that they do not appear to be specific to the field operations.

Three workers and two different areas were monitored in Area A during this survey. All of the personal monitoring results were below the limits of quantification (LOQ), both before and after Triazine addition. An area air sample at the Mill A sump indicated low levels of formaldehyde (< 100 ppb) after the addition of Triazine.

Three workers and three different areas were monitored in Area B during this survey. All personal and area air samples were below the LOQ prior to the addition of Triazine. Two of the three personal samples were detected near or above the 100 ppb level in the afternoon. Interestingly, all of the area and source air samples were well below these levels after the addition of Triazine.

Five air samples were taken on an employee and in areas when Triazine was added to the two metalworking fluid systems, and these were all below the LOQ.

The results of metalworking fluid analyses are displayed in Table V. The results indicate that Triazine levels were very low in Mill B, before and after the addition of Triazine. Triazine levels were much higher in Mill A, but formaldehyde levels were mostly below the LOQ in this area.

TABLE I
RESULTS OF FORMALDEHYDE MONITORING AT SITE #2
MILL A

SAMPLE TYPE	OPERATION	DURATION (min)	FORMALDEHYDE CONCENTRATION (PPB) REPORTED VALUE	CORRECTED VALUE
PRIOR TO THE ADDITION OF TRIAZINE				
Personal Air Samples				
Tube	Helper	223	< 19	
Tube	Operator	205	< 20	
Dosimeter	Helper	220	< 29	
Area Air Samples				
Impinger	On Operator's Desk	210	< 19	
Source Air Samples				
Impinger	Directly over Sump	213	< 19	
Tube	(duplicate sample)	213	39	32
Dosimeter	(duplicate sample)	213	< 30	
AFTER THE ADDITION OF TRIAZINE				
Personal Air Samples				
Tube	Helper	184	< 23	
Tube	Operator	182	< 25	
Dosimeter	Helper	183	< 35	
Area Air Samples				
Impinger	On Operator's Desk	208	< 19	
Source Air Samples				
Impinger	Directly over Sump	213	41	30
Tube	(duplicate sample)	213	73	60
Dosimeter	(duplicate sample)	213	< 30	
DURING THE ADDITION OF TRIAZINE				
Personal Air Samples				
Tube	On Employee Adding Triazine	5	< 930*	
Dosimeter	(duplicate sample)	5	<1250*	
Area Air Sample				
Impinger	On Ground Next to Triazine Addition	5	< 127	

* note: these very high LOQ values are due to the very short sample time (5 minutes).

TABLE II
RESULTS OF FORMALDEHYDE MONITORING AT SITE #2
MILL B

SAMPLE TYPE	OPERATION	DURATION (min)	FORMALDEHYDE CONCENTRATION (PPB) REPORTED VALUE	CORRECTED VALUE
PRIOR TO THE ADDITION OF TRIAZINE				
Personal Air Samples				
Tube	Operator	211	< 22	
Tube	Helper	211	< 21	
Dosimeter	Helper	210	< 30	
Area Air Samples				
Impinger	On Operator's Desk	207	< 20	
Dosimeter	(duplicate sample)	231	< 28	
Source Air Samples				
Impinger	Next to Sump	216	< 20	
Dosimeter	At exit end of Sump	216	< 31	
AFTER THE ADDITION OF TRIAZINE				
Personal Air Samples				
Tube	Operator	179	110	96
Dosimeter	Helper	181	< 31	
Dosimeter	Helper	180	96	84
Area Air Samples				
Impinger	On Operator's Desk	198	< 20	
Source Air Samples				
Impinger	Next to Sump	200	23	< 20
Dosimeter	At exit end of Sump	200	< 32	
Dosimeter	On floor next to Triazine Addition	217	< 30	
Dosimeter	(duplicate sample)	217	< 30	
DURING THE ADDITION OF TRIAZINE				
Personal Air Samples				
Tube	On Employee Adding Triazine	12	< 390	
Dosimeter	(duplicate sample)	12	< 540	

TABLE III
RESULTS OF FORMALDEHYDE MONITORING AT SITE #2
CONTROL SAMPLES

TYPE	OPERATION	DURATION (MIN)	FORMALDEHYDE CONCENTRATION (PPB)
Personal Air Samples			
These are air samples from employees working at operations not using metalworking fluid in the building which housed the two mills.			
Dosimeter	Edger Operator	210	< 31
Dosimeter	Mill Operator	208	< 31
Area Air Samples			
Impinger	On Edger Operator's desk	210	< 20
Dosimeter	(repeat sample)	182	< 35
Dosimeter	At Mill Operator's Desk	182	< 35
Tube	In Foreman's Office	203	< 23
Dosimeter	(repeat sample)	187	< 35

TABLE IV
RESULTS OF FORMALDEHYDE MONITORING AT SITE #2
FIELD RECOVERIES OF FORMALDEHYDE SPIKES

Sample Type	Area/Personal	Spike(μg)	Recovery (μg)	%Recovery
MILL A				
Tube	P	3	3.3	110
Tube	P	3	3.7	123
Tube	P	3	3.4	113
Tube	P	3	3.9	130
Tube	A	3	3.6	120
Tube	A	3	3.9	130
Summary of tubes: mean recovery= 121 s.d.= 8 n=6				
Impinger	A	30	44.6	149
Impinger	A	30	47.0	157
Summary of impingers: mean recovery= 153, n=2				
Dosimeter	P	1	1.5	150
MILL B				
Tube	P	3	3.5	116
Tube	P	3	3.7	123
Tube	P	3	3.0	100
Tube	P	3	3.5	116
Summary of tubes: mean recovery= 114 s.d.= 8 n=4				
Impinger	A	30	33.2	111
Impinger	A	30	40.6	135
Summary of impingers: mean recovery= 123, n=2				
Dosimeter	P	1	1.3	130
Dosimeter	P	1	0.9	90
Dosimeter	A	1	1.3	130
Summary of dosimeters: mean recovery = 117, s.d. = 19, n=3				
COMBINING ALL DOSIMETER AND IMPINGER RESULTS FOR MILLS A & B:				
Summary of Dosimeters: mean recovery = 125, s.d. = 25, n=4				
Summary of Impingers : mean recovery = 138 s.d.= 17, n=4				
FIELD BLANK SPIKES				
Tube	-	3	3.9	130
Tube	-	3	3.4	113
Tube	-	3	3.8	127
Summary of tubes: mean recovery = 123, s.d. = 7 , n=3				
Impinger	-	30	45.1	150
Impinger	-	30	31.5	105
Impinger	-	30	45.1	150
Summary of impingers: mean recovery = 135, s.d. = 21, n=3				
Dosimeter	-	1	1.5	150
Dosimeter	-	1	1.3	130
Dosimeter	-	1	1.6	160
Summary of dosimeters: mean recovery = 147, s.d. = 12, n=3				

TABLE V
SUMMARY OF ANALYSES OF COOLANT SAMPLES AT SITE #2

SYSTEM	pH	TEMP. (°F)	TRIAZINE (PPM)
Mill A: Pre-Addition	9.15	90	550
Mill A: Post-Addition	9.30	90	1240
Mill B: Pre-Addition	8.30	110	None Detected
Area B: Post-Addition	9.15	110	220

SITE #3

Summary

Two different metalworking operations were examined over two days at an automotive transmission plant. Each operation had its own central sump which supplied coolant to a variety of machines. The two operations were housed in separate facilities approximately one-half to one mile apart. A total of 114 air samples for formaldehyde were taken over a two day period. Sixty one of these samples were taken on workers, and 53 were placed in areas of the plant where exposure was likely. One operation, where Triazine levels in the metalworking fluid were very low (0-400 ppm), resulted in low levels of formaldehyde (<100 ppb) from air samples taken on workers and in areas. The second operation, where Triazine levels in the fluid were 1300-1400 ppb, resulted in samples with formaldehyde levels above 100 ppb. No employee received an exposure above the OSHA Action Level of 500 ppb.

Background

The third site visited in this study was an automotive transmission plant. A variety of different types of machining were performed on small to medium sized parts. Some operations were relatively well enclosed with little aerosolization of coolant at the employee's breathing zone, while others had no enclosure and the employee could inhale a significant amount of coolant over-spray.

Employees at this facility had been complaining in one area of eye, nose and throat irritation. We were asked to perform part of our survey in this area. For this report, this area will be identified as Area A. Operations in this area were very congested and there was very poor general exhaust ventilation. The area had a decay-like odor, and when Triazine was added an ammonia-type odor was off-gassed which did cause eye irritation. Because of employee complaints, a large number of personal air samples were taken at this operation. Since this survey encompassed two days, air samples were obtained overnight in Area A, after the addition of Triazine to monitor formaldehyde levels. The coolant system consisted of 16,000 gallons of water-soluble metalworking fluid. The sump was located in the general vicinity of most of the operations monitored. The sump was below ground level, but it was naturally ventilated into the operating area. During the study, an employee poured 16 gallons of concentrated Triazine directly into the sump.

A second operation was monitored at this facility, which will be identified as Area B. It was located in a separate building, next to Area A (approximately one-half to one mile away). Unlike Area A, the operations were far apart and there was no congestion. There were also windows around the building which were opened during most of the survey allowing for natural ventilation. The facility was maintaining this system by adding small quantities of Triazine on a daily basis, as opposed to approximately once a week in Area A. The employees had no complaints, and those working in Area A were hoping that their system could eventually be operated in a similar manner. The sump was located near two large machining operations and was considerably further from most other operations than the sump in Area A. Both areas had closed flumes which moved the coolant from the machines back to the sump. Every employee working in this area was monitored. The coolant system consisted of 18,000 gallons of a semi-synthetic coolant. Approximately two gallons of concentrated Triazine was added directly to the sump during this study.

Results

The results of all monitoring are shown in Tables I-IV. The results of monitoring the metalworking coolant are shown in Table V. All background samples were below the limits of quantification (LOQ) for the methods used, and no correction of the data for background levels of formaldehyde were made.

The results of recoveries of known levels of formaldehyde in field spikes are shown in Table IV. The data in Tables I and II are shown both as reported values and corrected for spiked recoveries. All spiked recoveries were greater than 100%, so the exposure data were reduced accordingly. It is clear from the data in Table IV that the standard deviations were significantly higher for values obtained in Area B over those from Area A. In addition, the dosimeter spikes were not very accurate and the correction factor was quite significant. It is possible that the dosimeters were not performing accurately in Area B, and this data must be judged accordingly.

Ten workers and three different areas were monitored in Area A during this survey. All of the personal monitoring resulted in values below the limits of quantification (LOQ) for the three methods used. All of these results were below 100 ppb, with the exception of the short-term samples taken during the addition of Triazine. These were also below the LOQ, and below the 2000 ppb STEL standard set by OSHA. Most area air samples were below the LOQ prior to the addition of Triazine. The addition of Triazine resulted in higher levels. The only area samples over 100 ppb were detected after the addition of Triazine directly over the sump. This was a source sample, and was not an area where employees would normally work. The dosimeter samples taken during the evening at two locations demonstrate that formaldehyde levels were decreasing, after the addition of Triazine.

Six workers and three areas were sampled in Area B. All employee samples were above 100 ppb, with the exception of one taken in the morning on the pipefitter. It should be noted, that this was a position which rotated throughout the plant, and he spent a significant portion of time away from where metalworking fluids were used (except for the short sample taken while at the sump). All personal samples were below the OSHA Action Level of 500 ppb, although one partial-shift sample on Machine Operator #1 approached this level. Observations suggested that Machine Operators #1 and #2, who worked together, received the highest aerosol concentration of metalworking fluid. The Maintenance Helper often had to go into machines to do repair work.

The results of metalworking fluid analyses are displayed in Table V. The results indicate that Triazine levels were never high in Area A. Triazine levels were very stable in Area B, consistent with the practice of daily additions of biocide.

TABLE I
RESULTS OF FORMALDEHYDE MONITORING AT SITE #3
AREA A

SAMPLE TYPE	OPERATION	DURATION (min)	FORMALDEHYDE CONCENTRATION (PPB) REPORTED VALUE	CORRECTED VALUE
PRIOR TO THE ADDITION OF TRIAZINE				
Personal Air Samples				
Tube	Heat Treat Operator	174	< 26	
Tube	Lathe Operator	172	< 26	
Dosimeter	Grinder #1	172	< 37	
Tube	Machining Operator #1	163	< 29	
Dosimeter	Machining Operator #2	166	< 39	
Tube	Machining Operator #3	158	< 28	
Dosimeter	Grinder #2	158	< 41	
Dosimeter	Machining Operator #4	146	< 44	
Dosimeter	Grinder #3	137	< 47	
Area Air Samples				
Impinger	Near Central Sump	143	< 28	
Tube	" " "	143	< 31	
Dosimeter	" " "	143	< 45	
Impinger	On Worktable in Center of Area A	137	< 30	
Source Area Air Sample				
This sample was taken directly over the sump next to an updraft.				
Impinger	Over Sump	138	< 30	
Tube	" "	138	< 32	
Dosimeter	" "	138	71	69
DURING THE ADDITION OF TRIAZINE				
Personal Air Samples				
Tube	On Employee Adding Triazine	18	< 248	
Dosimeter	" " "	18	< 360	
Area Air Sample				
Impinger	On Ground Next to Triazine Addition	18	< 225	

AFTER THE ADDITION OF TRIAZINE

Personal Air Samples

Dosimeter	Heat Treat Operator	117	< 55	
Tube	Lathe Operator	127	< 36	
Tube	Grinder #1	119	< 39	
Dosimeter	Machining Operator #1	115	< 56	
Tube	Machining Operator #2	121	< 37	
Tube	Machining Operator #3	109	< 41	
Dosimeter	Grinder #2	111	< 58	
Dosimeter	Machining Operator #4	118	< 55	
Dosimeter	Grinder #3	110	< 60	

Area Air Samples

Impinger	Near Central Sump	112	69	58
Tube	" " "	112	< 36	
Dosimeter	" " "	112	< 57	
Impinger	On Worktable in Center of Area A	123	75	63
Dosimeter (note:sample ran all night)	" " "	1061	59	57

Source Area Air Sample

This sample was taken directly over the sump next to an updraft.

Impinger	Over Sump	112	108	91
Tube	" "	112	77	68
Dosimeter	" "	112	180	175
Dosimeter (note: sample ran all night)	" "	1054	72	70

TABLE II
RESULTS OF FORMALDEHYDE MONITORING AT SITE #3
AREA B

SAMPLE TYPE	OPERATION	DURATION (min)	FORMALDEHYDE CONCENTRATION (PPB) REPORTED VALUE	CORRECTED VALUE
PRIOR TO THE ADDITION OF TRIAZINE				
Personal Air Samples				
Tube	Machine Operator #1	212	310	270
Dosimeter	Machine Operator #2	211	470	173
Dosimeter	Maint. Helper	206	250	92
Dosimeter	Machine Operator #3	194	160	59
Dosimeter	Machine Operator #4	195	320	118
Dosimeter	Pipefitter	223	62	< 29
Dosimeter	" " (short sample while working at sump)	47	140	< 137
Area Air Samples				
Impinger	Near Machine Opr. #1 and #2	200	188	155
Tube	" " " "	200	280	243
Dosimeter	" " " "	200	161	59
Impinger	Furthest Point From Sump	196	178	147
Dosimeter	" " "	196	< 33	
Source Area Air Sample				
Impinger	At Sump, Directly Over Return Flume	196	131	108
Tube	" "	196	210	183
Dosimeter	" "	196	270	99
DURING THE ADDITION OF TRIAZINE				
Personal Air Samples				
Tube	On Employee Adding Triazine	7	< 640	
Area Air Sample				
Impinger	On Ground Next to Triazine Addition	7	< 580	

AFTER THE ADDITION OF TRIAZINE

Personal Air Samples

Tube	Machine Operator #1	145	490	426
Dosimeter	Machine Operator #2	145	160	59
Dosimeter	Maint. Helper	146	410	151
Dosimeter	Machine Operator #3	149	140	51
Dosimeter	Machine Operator #4	144	270	99
Dosimeter	Pipefitter	157	340	125

Area Air Samples

Impinger	Near Machine Opr. #1 and #2	147	216	179
Tube	" " " "	147	320	278
Dosimeter	" " " "	147	< 44	
Impinger	Over Return Flume, Far From Sump	139	128	106
Tube	" " "	139	260	226

Source Area Air Sample

Impinger	At Sump, Directly Over Return Flume	143	179	148
Tube	" "	143	440	383
Dosimeter	" "	143	230	85

TABLE III
RESULTS OF FORMALDEHYDE MONITORING AT SITE #3
CONTROL SAMPLES

TYPE	OPERATION	DURATION (MIN)	FORMALDEHYDE CONCENTRATION (PPB)
These are all area air samples, taken in the building which housed operations described as Area "A".			
Dosimeter	Forklift Repair	135	< 48
Dosimeter	" "	114	< 56
Dosimeter	Battery Storage	136	< 47
Dosimeter	Battery Storage	114	< 56
Dosimeter	Foreman's Office	349	< 18

TABLE IV
RESULTS OF FORMALDEHYDE MONITORING AT SITE #3
FIELD RECOVERIES OF FORMALDEHYDE SPIKES

Sample Type	Area/Personal	Spike(μg)	Recovery (μg)	%Recovery
AREA A				
Tube	P	3	3.7	123
Tube	P	3	3.7	123
Tube	P	3	3.1	103
Tube	P	3	3.5	117
Tube	P	3	3.6	120
Tube	P	3	4.1	137
Tube	P	3	2.6	87
Tube	P	3	3.5	117
Tube	A	3	2.6	87
Summary of tubes: mean recovery= 113 s.d.= 16 n=9				
Impinger	A	33	40.2	122
Impinger	A	33	40.2	122
Impinger	A	33	38.8	118
Impinger	A	33	37.2	113
Summary of impingers: mean recovery= 119, s.d.= 4, n=4				
Dosimeter	P	1	1.1	110
Dosimeter	P	1	1.2	120
Dosimeter	P	1	1.0	100
Dosimeter	P	1	1.0	100
Dosimeter	P	1	1.1	110
Dosimeter	P	1	0.73	73
Dosimeter	P	1	1.1	110
Dosimeter	P	1	1.1	110
Dosimeter	P	1	1.0	100
Dosimeter	P	1	1.0	100
Summary of dosimeters: mean recovery = 103, s.d. = 12, n=10				
AREA B				
Tube	P	3	5.9	197
Tube	P	3	3.4	113
Tube	P	3	3.5	117
Tube	P	3	2.5	83
Tube	A	3	1.5	50
Tube	A	3	4.3	143
Tube	A	3	2.9	97
Tube	A	3	3.9	130
Tube	A	3	3.1	103
Summary of tubes: mean recovery= 115 s.d.= 39 n=9				
Impinger	A	33	39.1	118
Impinger	A	33	28.4	86
Impinger	A	33	45.9	140
Impinger	A	33	46.6	141

Summary of impingers: mean recovery= 121, s.d.= 22, n=4

Dosimeter	P	1	0.2	20
Dosimeter	P	1	1.8	180
Dosimeter	P	1	3.9	390
Dosimeter	P	1	6.1	610
Dosimeter	P	1	1.6	160

Summary of dosimeters: mean recovery = 272, s.d. =206, n=5

TABLE V
SUMMARY OF ANALYSES OF COOLANT SAMPLES AT SITE #3

SYSTEM	pH	TEMP. (°F)	TRIAZINE (PPM)
Area A: Pre-Addition	8.80	79	None Detected
Area A: Post-Addition	8.97	79	400
Area B: Pre-Addition	9.44	82	1300
Area B: Post-Addition	9.48	82	1400

SITE #4

Summary

Two different metalworking operations were examined over two days at a machinery manufacturer. The two operations shared a central sump which supplied coolant to a variety of machines. The two operations were housed in different segregated areas of the same large facility.

A total of 53 air samples for formaldehyde were taken at two different metalworking operations. Twenty two of these samples were taken on workers and 31 were placed in areas of the plant where exposure was likely. At the two different manufacturing operations, nine out of 10 different personal air samples taken indicated exposure above 100 ppb of formaldehyde. None of these values exceeded the OSHA Action Level of 500 ppb, and only one exceeded 200 ppb. All 13 area air samples indicated formaldehyde levels below 100 ppb. Two personal air samples taken during the addition of Triazine indicated levels below the LOQ. Two of the three methods used resulted in high levels of formaldehyde (above 500 ppb), when samples were taken at the coolant sump. It is not clear why the impinger method resulted in significantly different values than the other two methods. Triazine levels were very high in the metalworking coolant, over 1000 ppm to begin with and nearly 1700 ppm after the addition of biocide.

Background

The fourth site visited in this study was a manufacturer of large industrial machinery. A variety of different types of machining were performed on generally very large-sized parts. Most operations were relatively well enclosed with little aerosolization of coolant at the employee's breathing zone.

Area A consisted of four large machines which had parts brought in and taken out by robots. Only one employee worked directly around these machines, while another employee worked in the general area. Both of these workers were monitored along with several areas of the plant. There was no obvious mechanical ventilation in this area. The ceilings were about 20 feet high, and the return flumes to the sump were all covered.

Area B consisted of very large machines which performed a variety of complex cutting functions on large parts. The room was air conditioned to maintain a constant temperature and relative humidity, and the room had 40-50 foot high ceilings. There was an open flume several feet below ground which brought the coolant back to the sump. We monitored three of the employees working in this area and took several area air samples.

A large central sump containing approximately 20,000 gallons provided water-soluble coolant to these two areas. The sump was located outside the building housing these operations and was below ground. The sump was located in a small, approximately 15 by 30 foot space which was extremely poorly ventilated. The relative humidity in the sump was approximately 100% because of the lack of ventilation. Air samples were taken at the sump.

Samplers were placed on individuals and in areas in the morning and removed during lunchtime. At this time, an employee added 20 gallons of Triazine (four five-gallon pails) to the sump, by pouring it into a return flume by Area A. New samplers were then put on employees and back in areas for the remainder of the shift.

Two areas were selected as controls for this facility. One was inside a metallurgical laboratory, and the other in the plant manager's office. Both of these offices were part of the general building housing the two operations.

Results

The results of all monitoring are shown in Tables I-V. The results of monitoring the metalworking coolant are shown in Table VI. Two control samples indicate background formaldehyde levels of between 18 and 38 ppb. The results were corrected by subtracting 28 ppb (the average of the two background samples) from all samples taken in the production facility. Since the sump was located in an entirely different location, no background corrections were made for area air samples taken at this location.

Recoveries of known spiked quantities of formaldehyde are shown in Table V. The recoveries for each area were used to correct samples taken in those areas. The exception is for Area A, where impinger data from Area B was used, since there was no data for Area A. It is not clear whether some of these adjustments are warranted, given the very small number of spiked sampling data for some media and the widely different recoveries. This is why reported values (uncorrected values) continue to be listed in the table.

Two workers and two different locations were monitored in Area A during this survey. The area samples were all below 100 ppb both before and after the addition of Triazine. The machine operator's exposure was above 100 ppb before the addition of Triazine and rose to over 250 ppb after Triazine was added to the system. The other employee monitored at this location worked in the general area, but not nearly as close to the machines as the operator. This employee's exposure was much lower, but still exceeded 100 ppb after Triazine was added.

Three workers and three locations were monitored in Area B during this survey. All employee exposures were above 100 ppb both before and after the addition of Triazine. Formaldehyde levels increased in two of the three personal samples after Triazine was added. All areas monitored were below 100 ppb, and levels did not significantly fluctuate after the addition of Triazine.

Source samples at the sump indicated very high formaldehyde levels for both silica-gel tubes and dosimeters, while impinger samples indicated levels below 100 ppb. All three samplers indicated modestly higher levels after Triazine was added to the system. Personal samples taken on an employee adding Triazine indicated levels below the LOQ. One area sample taken where Triazine was added resulted in a short-term sample of 810 ppb.

Although the working conditions varied dramatically among operators in areas A and B, their exposures were of a similar magnitude in this study. All area air samples consistently resulted in levels below those obtained on employees, even when efforts to obtain maximum exposures were made. Samples taken inside the metalworking sump indicated generally high levels, but varied widely depending on the sampling media used. High humidity would be expected to make accurate monitoring difficult, although this does not necessarily explain the very low results obtained with impingers.

The results of relatively high recoveries from spiked blank samples, again suggests a positive interference which cannot be completely explained by workplace environmental conditions.

TABLE I
RESULTS OF FORMALDEHYDE MONITORING AT SITE #4
AREA A

SAMPLE TYPE	OPERATION	DURATION (min)	FORMALDEHYDE CONCENTRATION (PPB) REPORTED VALUE	CORRECTED VALUE
PRIOR TO THE ADDITION OF TRIAZINE				
Personal Air Samples				
Dosimeter	Worker in General Area	242	52	28
Tube	Machine Operator	211	154	119
Area Air Samples				
Impinger	In general area about ten feet from a machine	208	26	<20
Dosimeter	(duplicate sample)	208	83	57
Impinger	Directly next to a machine, approx. 6 feet off the ground	204	27	<20
Dosimeter	(duplicate sample)	204	< 32	
AFTER THE ADDITION OF TRIAZINE				
Dosimeter	Worker in General Area	162	106	84
Tube	Machine Operator	161	257	213
Area Air Samples				
Impinger	In general area about ten feet from a machine	202	33	<20
Impinger	Directly next to a machine, approx. 6 feet off the ground	202	80	47

TABLE II
RESULTS OF FORMALDEHYDE MONITORING AT SITE #4
AREA B

SAMPLE TYPE	OPERATION	DURATION (min)	FORMALDEHYDE CONCENTRATION (PPB) REPORTED VALUE	CORRECTED VALUE
PRIOR TO THE ADDITION OF TRIAZINE				
Personal Air Samples				
Tube	Machine Operator #1	236	137	109
Tube	Machine Operator #2	172	137	109
Tube	Machine Operator #3	230	122	101
Area Air Samples				
Impinger	On ground level, about four feet above open return flume	194	27	<21
Dosimeter	(duplicate sample)	194	61	<33
Impinger	At machine operator's desk, about five feet from a machine	191	<21	
Dosimeter	(duplicate sample)	191	67	<34
AFTER THE ADDITION OF TRIAZINE				
Personal Air Samples				
Tube	Machine Operator #1	154	163	133
Tube	Machine Operator #2	154	160	130
Dosimeter	Machine Operator #3	153	102	56
Area Air Samples				
Impinger	On ground level, about four feet above open return flume	194	26	<21
Dosimeter	(duplicate sample)	194	<33	
Dosimeter	At machine operator's desk, about five feet from a machine	188	70	<34

TABLE III
RESULTS OF FORMALDEHYDE MONITORING AT SITE #4
METALWORKING SUMP AND TRIAZINE ADDITION ACTIVITIES

SAMPLE TYPE	OPERATION	DURATION (min)	FORMALDEHYDE CONCENTRATION (PPB) REPORTED VALUE	CORRECTED VALUE
Area samples taken at the central sump about two to three feet directly above clean fume after it exited the filter.				
PRIOR TO THE ADDITION OF TRIAZINE				
Impinger	At central sump	214	77	45
Tube	(duplicate sample)	214	868	1173
Dosimeter	(duplicate sample)	214	479	319
AFTER THE ADDITION OF TRIAZINE				
Impinger	At central sump	207	97	56
Tube	(duplicate sample)	207	1290	1743
Dosimeter	(duplicate sample)	207	682	455
PERSONAL AND AREA AIR SAMPLES DURING THE ADDITION OF TRIAZINE				
Tube	Employee adding Triazine	14	<345	
Dosimeter	(duplicate sample)	14	<463	
Impinger	On ground next to Triazine addition	14	810	664

TABLE IV
RESULTS OF FORMALDEHYDE MONITORING AT SITE #4
CONTROL SAMPLES

TYPE	OPERATION	DURATION (MIN)	FORMALDEHYDE CONCENTRATION (PPB)
Dosimeter	In Plant Manager's office	436	38
Dosimeter	In Metallurgical Lab	418	18

TABLE V
RESULTS OF FORMALDEHYDE MONITORING AT SITE #4
FIELD RECOVERIES OF FORMALDEHYDE SPIKES

Sample Type	Area/Personal	Spike(μg)	Recovery (μg)	%Recovery
AREA A				
Tube	P	3	3.5	117
Tube	P	3	3.1	103
Summary of tubes: mean recovery = 110, n=2				
Dosimeter	P	1	1.1	110
Dosimeter	P	1	1.0	100
Summary of dosimeters: mean recovery= 105%, n=2				
AREA B				
Tube	P	3	3.6	120
Tube	P	3	2.7	90
Tube	P	3	2.6	87
Tube	P	3	3.2	107
Tube	P	3	3.6	120
Summary of tubes: mean recovery = 105, s.d. = 14, n=5				
Impinger	A	33	45.5	138
Impinger	A	33	34.5	105
Summary of impingers: mean recovery = 122, n=2				
CONTROL AREA				
Dosimeter	A	1	1.4	140
ADDING TRIAZINE TO METALWORKING FLUID				
Tube	P	3	3.8	127
AT CENTRAL SUMP				
Tube	A	3	2.0	67
Tube	A	3	2.4	80
Summary of tubes: mean recovery = 74%, n=2				
Impinger	A	33	43.7	132
Impinger	A	33	70.7	214
Summary of impingers: mean recovery = 173, n=2				
Dosimeter	A	1	1.5	150
Dosimeter	A	1	1.5	150
SPIKED BLANK SAMPLES				
Tube	-	1	1.33	133
Tube	-	1	1.12	112
Summary of tubes: mean recovery = 123, n=2				
Impinger	-	33	35.8	108
Impinger	-	33	44.6	135
Summary of impingers: mean recovery = 122, n=2				
Dosimeters	-	1	1.36	136
Dosimeters	-	1	1.65	165
Summary of dosimeters: mean recovery = 151, n=2				

TABLE VI
SUMMARY OF ANALYSES OF COOLANT SAMPLES AT SITE #4

SYSTEM	pH	TEMP. (°F)	TRIAZINE (PPM)
Pre-Addition	9.64	80-85	1045
Post-Addition	9.68	80-85	1685

SITE #5

Summary

A group of seven different employees engaged in machining and grinding moderate-sized parts was examined. All employees worked in close proximity to each other. The five machining operations were all directly connected to a central sump. Two grinding operations had self-contained systems which were periodically replenished from the central sump.

A total of 62 air samples for formaldehyde were taken at this facility. Thirty eight of these samples were taken on workers and 24 were placed in areas of the plant, where exposure was likely. The two control samples indicated substantial levels of formaldehyde where no Triazine was present. An average value of 78 ppb was used to correct the data along with the average recoveries from spiked samples taken at various locations.

When the data is corrected for background contamination and recoveries, only one of the 12 personal air samples and none of the area samples were above 100 ppb. If uncorrected data is considered then nine of the 12 personal air samples and one of 13 area air samples were above 100 ppb. Air samples taken inside a poorly ventilated sump indicated formaldehyde levels above 500 ppb. This is not an area that would have any employees present except to take coolant samples or perform maintenance activities.

Background

The fifth site visited in this study was a manufacturer of medium-sized industrial machinery. A variety of different types of machining were performed on generally varied-sized parts. Approximately 15 different machines using metalworking coolant operated within a single undivided building space, and many operations monitored were adjacent to each other. Most machines used a coolant from a single central sump located outside the building.

Seven different employees operating five machines and two grinders were monitored. The two grinding machines had self-contained coolant systems which were changed as needed. The coolant came from the central system, and waste coolant was added back to the central system. As was the case for the other sites, sampling was done in the morning and samples were changed during a lunch break. In between sampling, 20 gallons of Triazine was added to the central system through a return flume. At approximately the same time, eight ounces of Triazine were added to the coolant system used by Grinder #1, and the entire coolant system for Grinder #2 was exchanged with fresh coolant from the central system.

Most of the manufacturing operations were enclosed, but the two grinding operations and machining operations done by Operators #1 and #2 were not enclosed. The operation done by Machine Operator #1 was particularly notable in spraying coolant into the air and over the floor. All return flumes to the central sump were enclosed.

The central sump contained 20,000 gallons of semi-synthetic water-soluble coolant. It was located below ground level outside of the manufacturing building. The room containing the sump had no mechanical and little natural ventilation, and had approximately 100% relative humidity. The air in the sump room appeared to be mildly irritating to the eye, but with no noticeable odor.

Two locations were monitored for background levels of formaldehyde. One was the supervisor's office and the other was inside a conference room. Although both locations were within the manufacturing building, neither was adjacent to the operations monitored.

Due to a misunderstanding with the employee adding Triazine, no personal or area air monitoring was done during the addition process.

Results

The results of all monitoring are shown in Tables I-III. The results of monitoring the metalworking coolant are shown in Table IV. Two control samples indicated background formaldehyde levels of between 48 and 108 ppb. The results were corrected by subtracting 78 ppb (the average of the two background samples) from all samples taken in the production facility. Since the sump was located in an entirely different location, no background corrections were made for area air samples taken at this location. These are the highest background values found in this survey. It is not clear whether the office environments monitored as background are appropriate, however, formaldehyde levels in the production areas appeared to be potentially influenced by the metalworking fluid in use.

Recoveries of known spiked quantities of formaldehyde are shown in Table III. The recoveries for each area were used to correct samples taken in those areas. Data for silica-gel tubes and impingers showed good recoveries with relatively low standard deviations.

Twenty four (excluding spiked samples) personal air samples were taken on the seven workers monitored at this site. The data is highly influenced by whether corrected or reported values are used. If corrected values are used, only one of 12 samples taken prior to the addition of Triazine and only three of 12 samples taken after the addition of Triazine were above 100 ppb. None of these values exceeded 200 ppb. If uncorrected data are considered, nine of 12 values prior to the addition of Triazine were above 100 ppb and all samples after the addition of Triazine were above 100 ppb. In this case, all values were below 300 ppb of formaldehyde. Regardless of the choice of data set used, six of the seven employees monitored after the addition of Triazine had higher exposures to formaldehyde.

Thirteen different air samples were taken in various areas of the production facility. All six samples taken prior to the addition of Triazine were below 100 ppb, and only one of seven samples taken after the addition of Triazine was above 100 ppb. The effect of correcting these values for background levels and recoveries are that all areas of the facility become below the LOQ. There is no clear indication with this data that formaldehyde levels were rising in the afternoon, after the addition of Triazine to the metalworking fluid.

The two air samples taken inside the sump showed high levels of formaldehyde, between 500 and 1000 ppb. This is consistent with the results obtained at Site #4 where a sump was very poorly ventilated.

The results in Table IV indicate that the two grinders had essentially no Triazine in their fluid during the first sampling period. However, their exposures were comparable to the other employees. This may be due to the close proximity of all machines to each other. A visual observation indicated that Operator #1 was exposed to the most amount of metalworking fluid mist, yet formaldehyde exposures were no higher than fellow workers.

TABLE I
RESULTS OF FORMALDEHYDE MONITORING AT SITE #5

SAMPLE TYPE	OPERATION	DURATION (min)	FORMALDEHYDE CONCENTRATION (PPB) REPORTED VALUE	CORRECTED VALUE
PRIOR TO THE ADDITION OF TRIAZINE				
Personal Air Samples				
Tube	Grinder Operator #1	220	110	30
Dosimeter	(duplicate sample)	220	93	<29
Tube	Machine Operator #1	218	113	33
Dosimeter	(duplicate sample)	218	97	<29
Tube	Grinder Operator #2	217	130	50
Dosimeter	(duplicate sample)	217	105	<29
Tube	Machine Operator #2	212	162	80
Dosimeter	(duplicate sample)	212	114	<30
Tube	Machine Operator #3	212	207	123
Dosimeter	(duplicate sample)	212	107	<30
Dosimeter	Machine Operator #4	210	147	52
Dosimeter	Machine Operator #5	197	55	<33
Area Air Samples				
Impinger	On Operator's desk, About five feet from machine	163	30	<25
Impinger	On table near Machine Operator #1	165	45	<25
Impinger	On desk, in center area of machining operations	165	51	<25
Dosimeter	(duplicate sample)	165	97	<25
Impinger	On desk, near center area of machining operations	165	50	<25
Impinger	About five feet above grating for return flume	163	62	<25
Source Air Samples				
Dosimeter	Inside central sump, about five feet above flume	164	707	589

SAMPLE TYPE	OPERATION	DURATION (min)	FORMALDEHYDE CONCENTRATION (PPB) REPORTED VALUE	CORRECTED VALUE
AFTER THE ADDITION OF TRIAZINE				
<u>Personal Air Samples</u>				
Tube	Grinder Operator #1	171	170	88
Dosimeter	(duplicate sample)	171	149	54
Tube	Machine Operator #1	196	160	78
Dosimeter	(duplicate sample)	196	153	71
Tube	Grinder Operator #2	195	196	112
Dosimeter	(duplicate sample)	195	141	47
Tube	Machine Operator #2	196	250	164
Dosimeter	(duplicate sample)	196	185	80
Tube	Machine Operator #3	194	228	143
Dosimeter	(duplicate sample)	194	149	53
Dosimeter	Machine Operator #4	190	123	43
Dosimeter	Machine Operator #5	189	119	<34
<u>Area Air Samples</u>				
Impinger	On Operator's desk, About five feet from machine	208	43	<20
Impinger	On table near Machine Operator #1	207	35	<20
Dosimeter	(duplicate sample)	207	85	<31
Impinger	On desk, in center area of machining operations	206	74	<20
Dosimeter	(duplicate sample)	206	79	<31
Impinger	On desk, near center area of machining operations	206	85	<20
Impinger	About five feet above grating for return flume	205	104	<20
<u>Source Air Samples</u>				
Dosimeter	Inside central sump, about five feet above flume	269	890	742

TABLE II
RESULTS OF FORMALDEHYDE MONITORING AT SITE #5
CONTROL SAMPLES

TYPE	OPERATION	DURATION (MIN)	FORMALDEHYDE CONCENTRATION (PPB)
Dosimeter	In Supervisor's office	469	108
Dosimeter	In Conference Room	457	48

TABLE III
RESULTS OF FORMALDEHYDE MONITORING AT SITE #5
FIELD RECOVERIES OF FORMALDEHYDE SPIKES

Sample Type	Area/Personal	Spike(μg)	Recovery (μg)	%Recovery
OPERATING AREA				
Tube	P	3	3.3	110
Tube	P	3	3.3	110
Tube	P	3	2.0	67
Tube	P	3	3.8	127
Tube	P	3	3.0	100
Tube	P	3	3.3	110
Tube	P	3	3.0	100
Tube	P	3	2.9	97
Tube	P	3	3.7	123
Tube	P	3	3.3	110
Summary of tubes: mean recovery = 105, s.d.= 16, n=10				
Dosimeter	P	1	0.8	80
Dosimeter	P	1	1.7	170
Dosimeter	P	1	1.0	100
Dosimeter	P	1	1.8	180
Summary of dosimeters: mean recovery = 133, s.d. = 43, n=4				
Impinger	A	33	32.8	99
Impinger	A	33	34.2	104
Impinger	A	33	36.9	112
Impinger	A	33	32.8	99
Summary of impingers: mean recovery = 104, s.d. =5, n=4				
CENTRAL SUMP				
Dosimeter	A	1	1.4	140
Dosimeter	A	1	1.0	100
Summary of dosimeters: mean recovery = 120, n= 2				
CONTROL AREAS				
Dosimeter	A	1	0.9	90

TABLE IV
SUMMARY OF ANALYSES OF COOLANT SAMPLES AT SITE #5

SYSTEM	pH	TRIAZINE (PPM)
Central System		
Pre-Addition	9.43	586
Post-Addition	9.68	1012
Grinder #1 System		
Pre-Addition	8.40	None Detected
Post-Addition	9.68	1107
Grinder #2 System		
Pre-Addition	8.16	None Detected
Post-Addition	9.31	839

SITE #6

Summary

Two distinctly different operations were examined in an automotive manufacturer. One operation employed four persons machining parts, and another involved two employees grinding parts. These two different operations were supported by different metalworking systems, both of which used synthetic coolants.

All personal and area air samples for both operations, prior to the addition of Triazine indicated levels of formaldehyde below 100 ppb. A number of both personal and area air samples indicated levels above 100 ppb in the afternoon at the machining operations. All personal samples and all but one area air sample indicated levels below 100 ppb in the grinding operation.

An average background of 26 ppb of formaldehyde was detected in the main production area, and this value was used to correct air samples. Of the 37 personal air samples taken, only five were above 100 ppb, and none exceeded 500 ppb. Of the 29 area air samples taken, only four were above 100 ppb, and none exceeded 400 ppb. If the background level of formaldehyde is subtracted from these values, all nine samples above 100 ppb, with the exception of one personal air sample, remain above 100 ppb.

Background

The sixth site visited in this study was another automotive manufacturer. A variety of different types of machining and grinding occurred on small to medium-sized parts. All operations at this facility were housed in one large building. Two distinctly different operations were monitored at this location. Area A consisted of two rows of machines with a set-up person and operator for each row. The set-up person was observed occasionally machining parts. The location had very high ceilings (50-60 feet) and make-up air was introduced into the middle walkway, between the two rows of machines. Only one of the machines had any exhaust ventilation over it. This operation was supported by a below-ground sump which was 30-40 feet away. All return flumes were covered. The metalworking fluid used was synthetic and the sump contained 30,000 gallons. Fifty gallons of Triazine was added to the sump during the middle of this survey. The sump itself was poorly ventilated and appeared to contain about 100% relative humidity. During the afternoon, the overall workload was obviously less, and employees took breaks away from their worksite.

Area B consisted of a long row of grinding machines. Two employees operated them, one working on the back half closer to the sump, and the other on the front half. The ceilings were lower, about 25-35 feet high. There were local-exhaust ventilation hoods over each grinder, but there was no apparent make-up air to the area. The sump was again about 30-40 feet away, but was completely open at the top with much better natural ventilation. The metalworking system consisted of 20,000 gallons of a synthetic coolant. Approximately 25 gallons of Triazine was added to it during the day.

Four different locations were monitored for background levels of formaldehyde. These included two locations in about the middle of the facility, away from any immediate metalworking operation. The other two locations were in the chemist's office and in the cafeteria.

Two employees were monitored during the addition of Triazine and one area sample was taken. These samples represented the addition of Triazine to both metalworking fluid systems.

Due to a technical problem, there were no spiked samples taken in the field, but there were a number of duplicate samples taken.

Results

The results of all monitoring are shown in Tables I-V. The results of monitoring the metalworking coolant are shown in Table VI. Four control samples indicate background formaldehyde levels ranging from less than the LOQ to 30 ppb. The two control samples taken in the plant were averaged, and the results were corrected by subtracting 26 ppb from all samples taken in the production facility.

A total of 37 personal air samples and 29 area air samples were taken during this survey. All samples in Area A, taken on both workers and in area, were below the LOQ prior to the addition of Triazine to the metalworking fluid system. Five of the eleven personal air samples taken after the addition of Triazine were above 100 ppb, and all were below the OSHA Action Level of 500 ppb. Three of the seven samples taken in areas were above 100 ppb, but none were above 400 ppb. All four personal samples and one of the area air samples in the afternoon indicated significantly different values among the various duplicate samples. For example, each of the personal air samples had at least one of the values above 100 ppb and at least one below 100 ppb. This makes interpretation of the data more difficult. Workers in this area performed significantly less machining in the afternoon, than in the morning. This partially explains some of the short sample times in the afternoon, when two of the workers did not report back to their operations for nearly two hours.

All 12 air samples from workers and areas in Area B, prior to the addition of Triazine, were below the LOQ. Only one area air sample in the afternoon was above 100 ppb. All air samples taken from employees and in areas where Triazine was added indicated results below the LOQ.

Correcting the results for background contamination of formaldehyde produced very little change. Of the eight air samples above 100 ppb taken in Area A, seven remained above 100 ppb. The one sample above 100 ppb in Area B also remained above this limit after the correction was applied.

Since spiked recovery samples were not taken in this survey, we had the opportunity to examine precision among duplicate samples taken with the same type of monitor. The results of this comparison are shown in Table VI. Three of the four samples taken with silica-gel tubes were below the LOQ in both sets of tubes. In two of the eight pairs examined, one sample was above 100 ppb and one was below this value. In the case of dosimeters, five of the six devices which reported results below the LOQ had duplicates also below the LOQ. In only one of nine pairs examined, did one device indicate a level above 100 ppb and another below 100 ppb. The four pairs of impinger samples also showed good agreement among them.

The results of coolant analyses are displayed in Table VI. It can be seen for both systems that very low levels of Triazine existed in the morning and dramatically higher levels occurred after the addition of Triazine in the afternoon. This explains the obvious increase in formaldehyde levels in almost all samples taken in the afternoon when compared to those taken in the morning.

TABLE I
RESULTS OF FORMALDEHYDE MONITORING AT SITE #6
AREA A

SAMPLE TYPE	OPERATION	DURATION (min)	FORMALDEHYDE CONCENTRATION (PPB) REPORTED VALUE	CORRECTED VALUE
PRIOR TO THE ADDITION OF TRIAZINE				
Personal Air Samples				
Tube	Machine Operator #1	236	< 18	
Tube	(duplicate sample)	236	< 19	
Dosimeter	(duplicate sample)	236	< 27	
Dosimeter	Machine Operator #2	232	< 30	
Dosimeter	(duplicate sample)	218	< 30	
Tube	Set-Up Operator #1	237	< 18	
Tube	(duplicate sample)	237	< 19	
Dosimeter	(duplicate sample)	237	< 27	
Tube	Set-Up Operator #2	236	< 19	
Tube	(duplicate sample)	236	< 19	
Dosimeter	(duplicate sample)	236	< 27	
Area Air Samples				
Dosimeter	In aisleway, about four feet off the ground, near machines run by Operator #1	189	< 34	
Dosimeter	(duplicate sample)	189	< 34	
Impinger	About five feet off the ground, near machines run by Operator #2	195	< 21	
Dosimeter	(duplicate)	195	< 33	
Source Air Samples				
Impinger	Inside sump room	196	< 28	
Impinger	(duplicate sample)	196	< 28	
Dosimeter	(duplicate sample)	196	< 33	
AFTER THE ADDITION OF TRIAZINE				
Personal Air Samples				
Tube	Machine Operator #1	171	< 25	
Tube	(duplicate sample)	171	140	114
Dosimeter	(duplicate sample)	171	71	45

Dosimeter	Machine Operator #2	104	< 62	
Dosimeter	(duplicate sample)	104	160	134
Tube	Set-Up Operator #1	108	120	94
Tube	(duplicate sample)	108	72	46
Dosimeter	(duplicate sample)	108	140	114
Tube	Set-Up Operator #2	171	59	33
Tube	(duplicate sample)	171	53	27
Dosimeter	(duplicate sample)	171	410	384

<u>Area Air Samples</u>

Dosimeter	In aisleway, about four feet off the ground, near machines run by Operator #1	175	130	104
Dosimeter	(duplicate sample)	175	140	114
Impinger	About five feet off the ground, near machines run by Operator #2	171	< 25	
Dosimeter	(duplicate)	171	64	38

<u>Source Air Samples</u>

Impinger	Inside sump room	171	< 33	
Impinger	(duplicate sample)	171	61	35
Dosimeter	(duplicate sample)	196	320	294

TABLE II
RESULTS OF FORMALDEHYDE MONITORING AT SITE #6
AREA B

SAMPLE TYPE	OPERATION	DURATION (min)	FORMALDEHYDE CONCENTRATION (PPB) REPORTED VALUE	CORRECTED VALUE
PRIOR TO THE ADDITION OF TRIAZINE				
Personal Air Samples				
Tube	Grinder Operator #1	208	36	< 21
Tube	(duplicate sample)	208	30	< 21
Dosimeter	(duplicate sample)	208	< 30	
Dosimeter	Grinder Operator #2	207	< 30	
Dosimeter	(duplicate sample)	207	< 32	
Area Air Samples				
Impinger	Behind grinding machines near Operator #1, about 5-6 feet off ground	194	36	< 21
Dosimeter	(duplicate sample)	194	39	< 33
Dosimeter	In main walkway in front of machines near Operator #2, about 5 feet high	192	< 33	
Dosimeter	(duplicate)	192	< 33	
Source Air Samples				
Impinger	Inside sump area about three feet from flume	202	< 27	
Impinger	(duplicate sample)	202	< 27	
Dosimeter	(duplicate sample)	196	36	< 33
AFTER THE ADDITION OF TRIAZINE				
Personal Air Samples				
Tube	Grinder Operator #1	175	50	< 25
Tube	(duplicate sample)	175	58	32
Dosimeter	(duplicate sample)	175	43	< 37
Dosimeter	Grinder Operator #2	178	45	< 37
Dosimeter	(duplicate sample)	178	56	< 37
Area Air Samples				
Impinger	Behind grinding machines near Operator #1, about 5-6 feet off ground	169	45	< 24
Dosimeter	(duplicate sample)	169	150	124
Dosimeter	In main walkway in front of machines near Operator #2, about 5 feet high	173	41	< 37
Dosimeter	(duplicate)	173	54	< 37

<u>Source Air Samples</u>

Impinger	Inside sump area about three feet from flume	170	< 32
Impinger	(duplicate sample)	170	< 32
Dosimeter	(duplicate sample)	170	< 38

TABLE III
RESULTS OF FORMALDEHYDE MONITORING AT SITE #6
SHORT-TERM SAMPLES DURING THE ADDITION OF TRIAZINE

SAMPLE TYPE	OPERATION	DURATION (min)	FORMALDEHYDE CONCENTRATION (PPB) REPORTED VALUE	CORRECTED VALUE
Personal Air Samples				
Tube	Employee #1	27	<165	
Tube	(duplicate sample)	27	<165	
Dosimeter	(duplicate sample)	27	<238	
Dosimeter	Employee #2	27	<238	
Dosimeter	(duplicate sample)	27	<238	
Area Air Sample				
Impinger	On the ground next to Triazine addition at both sumps	12	<355	

TABLE IV
RESULTS OF FORMALDEHYDE MONITORING AT SITE #6
CONTROL SAMPLES

TYPE	OPERATION	DURATION (MIN)	FORMALDEHYDE CONCENTRATION (PPB)
Dosimeter	In Middle of plant location #1	431	30
Dosimeter	In Middle of plant location #2	427	22
Dosimeter	In chemist's office	432	< 15
Dosimeter	In cafeteria	408	< 16

TABLE V
RESULTS OF FORMALDEHYDE MONITORING AT SITE #6
COMPARISON OF DUPLICATE SAMPLES-IDENTICAL MONITORS

TYPE	PERSONAL/AREA	RESULTS (PPB)	% DIFFERENCE
Tube	P	< 18, < 19	-
Tube	P	< 18, < 19	-
Tube	P	< 25, 140	91
Tube	P	120, 72	60
Tube	P	59, 53	10
Tube	P	36, 30	17
Tube	P	50, 58	14
Tube	P	<165, <165	-
Summary: average difference= 38%, s.d. = 32, n=5			
Dosimeter	P	< 30, < 30	-
Dosimeter	A	< 34, < 34	-
Dosimeter	P	< 62, 160	80
Dosimeter	A	130, 140	7
Dosimeter	P	< 30, < 32	-
Dosimeter	A	< 33, < 33	-
Dosimeter	P	45, 56	20
Dosimeter	A	41, 54	24
Dosimeter	P	<238, <238	-
Summary: average difference= 33%, s.d. = 28, n=4			
Impinger	A	< 28, < 28	-
Impinger	A	< 33, 61	71
Impinger	A	< 27, < 27	-
Impinger	A	< 32, < 32	-

TABLE VI
SUMMARY OF ANALYSES OF COOLANT SAMPLES AT SITE #6

SYSTEM	pH	TRIAZINE (PPM)
Area A System		
Pre-Addition	9.20	169
Post-Addition	9.24	1894
Area B System		
Pre-Addition	8.96	301
Post-Addition	9.04	1847

SITE #7

Summary

A total of 58 air samples for formaldehyde were taken at a manufacturer of aluminum beverage cans. Eight different employees and six different areas were monitored during the survey. Triazine concentrations in the metalworking fluid were approximately 1000 ppm both before and after the addition of Triazine. Background levels of formaldehyde in the plant averaged 118 ppb, and there were several known sources in addition to the presence of Triazine. If background levels are not corrected from the data, virtually all the personal air sampling data (26/27 samples) exceeded 100 ppb. However, if the background level is subtracted, none of these samples exceeded 100 ppb. There is evidence at this facility that operations not involving metalworking fluids had higher levels of formaldehyde, further supporting the need to correct exposure data for background levels of formaldehyde.

Background

The seventh site visited in this study was an aluminum can manufacturer. The facility begins with coils of aluminum and finishes with aluminum cans which have already been printed with the manufacturer's name and logo. The basic operations which use metalworking fluid involve aluminum parts which are drawn and ironed into cans (known as D&I). This involved a number of machines performing different mechanical activities on the aluminum stock. The operation was supported by a 5,000 gallon sump containing a water-soluble coolant. The sump was located nearby the D&I operations and had a Schneider 10-plate filtering system. An isothiazolinone-based biocide was added daily to the system, and two gallons of Triazine was normally added twice weekly. Many operations observed had coolant visibly spraying in the air, and the return flumes were not covered.

We monitored four employees working in D&I, and one employee working in a wash department directly above D&I. Similar to other facilities, samplers were placed on employees and areas in the morning, the samples were removed approximately three hours later, Triazine was added to the metalworking system, and new samplers placed on the same employees and areas. One employee was monitored during the addition of Triazine and one area sample was taken. Two workers operating at a palletizer, far removed from this operation, served as background samples along with an area sample. The facility uses many printing inks and other solvents, some of which were labelled as warning about formaldehyde emissions.

Due to a technical problem, there were no spiked samples taken in the field, but there were a number of duplicate samples taken.

Results

The results of all monitoring are shown in Tables I-IV. The results of monitoring the metalworking coolant are shown in Table V. Eleven different background samples indicated formaldehyde levels ranging from 80-135 ppb. The average of all of these values was 118 ppb, and the results were corrected by subtracting this value from all samples taken in the production facility. This was by far the largest value obtained in any of the surveys, and correcting for this level has a dramatic effect on the results. Samples in the sump area, which was somewhat segregated in a corner from the rest of the production area, were very low and a correction may not be appropriate for these samples.

A total of 31 personal air samples and 21 area air samples were taken during this survey. Twenty six of the 27 personal air samples taken in the D&I area exceeded 100 ppb and ranged from 96-196 ppb. If the background formaldehyde value of 118 ppb is subtracted from these results, none of the samples exceeded 100 ppb. Eleven of the 14 area air samples taken at D&I and at the sump were below 100 ppb. Correcting for background only changes one of the three values above 100 ppb, to below this level. Nine of the 11 background samples were above 100 ppb. The palletizing area uses no chemicals and is simply a mechanical operation. The large percentage of samples above 100 ppb at other locations, strongly suggests that most of the formaldehyde measured in the plant was coming from sources and locations not using metalworking fluid, including inks and other wash products.

Since spiked recovery samples were not taken in this survey, we again had the opportunity to examine precision among duplicate samples taken with the same type of monitor. The results of this comparison are shown in Table IV. Both silica-gel tubes and dosimeter duplicate samples showed excellent agreement, indicating that both of these methods are capable of providing precise data.

The results of coolant analyses are displayed in Table V. The facility maintained very consistent levels of Triazine at or near 1000 ppm. There was no obvious increase in formaldehyde levels in the samples taken in the afternoon, and this is consistent with the relatively steady level of Triazine in the metalworking fluid.

TABLE I
RESULTS OF FORMALDEHYDE MONITORING AT SITE #7

SAMPLE TYPE	OPERATION	DURATION (min)	FORMALDEHYDE CONCENTRATION (PPB) REPORTED VALUE	CORRECTED VALUE
PRIOR TO THE ADDITION OF TRIAZINE				
Personal Air Samples				
Tube	D&I Operator #1	209	189	71
Tube	(duplicate sample)	209	196	78
Dosimeter	(duplicate sample)	209	150	< 31
Tube	D&I Operator #2	195	165	47
Tube	(duplicate sample)	195	166	48
Dosimeter	(duplicate sample)	195	127	< 33
Tube	D&I Operator #3	206	148	30
Tube	(duplicate sample)	206	168	50
Dosimeter	(duplicate sample)	206	127	< 31
Dosimeter	D&I Operator #4	195	121	< 33
Dosimeter	(duplicate sample)	195	143	< 33
Tube	Washer Operator	194	175	57
Tube	(duplicate sample)	194	175	57
Dosimeter	(duplicate sample)	194	139	< 33
Area Air Samples				
Impinger	On operator's desk In D&I area	189	24	< 21
Dosimeter	On platform over Draw machine	190	294	176
Source Air Samples				
Impinger	Directly over Sump	191	27	< 21
Dosimeter	(duplicate sample)	191	78	< 33
Dosimeter	(duplicate sample)	191	73	< 33
Impinger	Next to Schneider Filters	195	56	< 21
Dosimeter	(duplicate sample)	195	208	90

AFTER THE ADDITION OF TRIAZINE

Personal Air Samples

Tube	D&I Operator #1	277	128	< 16
Tube	(duplicate sample)	277	162	44
Dosimeter	(duplicate sample)	277	115	< 23
Tube	D&I Operator #2	262	155	37
Tube	(duplicate sample)	262	165	47
Dosimeter	(duplicate sample)	262	131	< 25
Tube	D&I Operator #3	270	115	< 17
Tube	(duplicate sample)	270	141	23
Dosimeter	(duplicate sample)	270	108	< 24
Dosimeter	D&I Operator #4	264	096	< 25
Dosimeter	(duplicate sample)	264	123	< 25
Tube	Washer Operator	284	121	< 16
Tube	(duplicate sample)	284	127	< 16
Dosimeter	(duplicate sample)	284	126	< 23

Area Air Samples

Impinger	On operator's desk In D&I area	290	49	< 14
Dosimeter	On platform over Draw machine	290	360	242

Source Air Samples

Impinger	Directly over Sump	296	26	< 14
Dosimeter	(duplicate sample)	296	83	< 21
Dosimeter	(duplicate sample)	296	67	< 21
Impinger	Next to Schneider Filters	299	17	< 14
Dosimeter	(duplicate sample)	299	58	< 21

TABLE II
RESULTS OF FORMALDEHYDE MONITORING AT SITE #7
SHORT-TERM SAMPLES DURING THE ADDITION OF TRIAZINE

SAMPLE TYPE	OPERATION	DURATION (min)	FORMALDEHYDE CONCENTRATION (PPB) REPORTED VALUE	CORRECTED VALUE
Personal Air Samples				
Tube	Employee adding two gallons of Triazine to the sump	9	<503	
Tube	(duplicate sample)	9	<503	
Dosimeter	(duplicate sample)	9	<726	
Dosimeter	(duplicate sample)	9	<726	

TABLE III
RESULTS OF FORMALDEHYDE MONITORING AT SITE #7
CONTROL SAMPLES

TYPE	OPERATION	DURATION (MIN)	FORMALDEHYDE CONCENTRATION (PPB)
PRIOR TO THE ADDITION OF TRIAZINE			
Dosimeter	Palletizer #1	205	133
Dosimeter	(duplicate sample)	205	135
Dosimeter	Palletizer #2	197	101
Dosimeter	(duplicate sample)	197	131
AFTER THE ADDITION OF TRIAZINE			
Dosimeter	Palletizer #1	266	123
Dosimeter	(duplicate sample)	266	118
Dosimeter	Palletizer #2	276	80
Dosimeter	(duplicate sample)	276	89
Dosimeter	In middle of building about 5 feet high	505	114
Dosimeter	(duplicate sample)	505	111
Dosimeter	In Palletizer Area	485	158

TABLE IV
RESULTS OF FORMALDEHYDE MONITORING AT SITE #7
COMPARISON OF DUPLICATE SAMPLES-IDENTICAL MONITORS

TYPE	PERSONAL/AREA	RESULTS (PPB)	% DIFFERENCE
Tube	P	189, 196	3
Tube	P	165, 166	1
Tube	P	148, 168	12
Tube	P	175, 175	0
Tube	P	128, 162	21
Tube	P	155, 165	6
Tube	P	115, 141	18
Tube	P	121, 127	5
Tube	P	<503, <503	-
Summary: average difference= 8%, s.d. = 7, n=8			
Dosimeter	P	121, 143	15
Dosimeter	A	78, 73	6
Dosimeter	P	96, 123	22
Dosimeter	A	83, 67	19
Dosimeter	P	<726, <726	-
Dosimeter	P	133, 135	2
Dosimeter	P	101, 131	23
Dosimeter	P	118, 123	4
Dosimeter	P	114, 111	3
Summary: average difference= 11%, s.d. = 8, n=8			

TABLE V
SUMMARY OF ANALYSES OF COOLANT SAMPLES AT SITE #7

SYSTEM	pH	TRIAZINE (PPM)
Pre-Addition	8.98	997
Post-Addition	8.93	1160

SITE #8

Summary

A total of 40 air samples for formaldehyde were taken at a manufacturer of aluminum beverage cans. Five different employees and five different areas were monitored during the survey. There were two different metalworking fluid systems which supported the production operations monitored. Triazine concentrations in the metalworking fluids were approximately 1000 ppm in one system and 1800 ppm in the other. Background levels of formaldehyde in the plant averaged 50 ppb, and there were several known sources of formaldehyde in addition to the presence of Triazine. If background levels are not corrected from the data, 22 of the 25 personal air sampling data exceeded 100 ppb. If the background level is subtracted, 13 of these samples exceeded 100 ppb. Six of the seven areas monitored were above 100 ppb, and three remained above 100 ppb after correcting for a background level of 50 ppb.

Background

The eighth and final site visited in this study was another aluminum can manufacturer. The facility also started with coils of aluminum and finishes with aluminum cans which were printed with the manufacturer's name and logo. The basic operations which use metalworking fluid involved aluminum parts which were drawn and ironed into cans (known as D&I).

There were a number of differences between the D&I and supporting metalworking fluid operations from Site #7 and this facility. There were 20 different machines using metalworking fluid on the D&I platform. Ten of the machines were on one side and were supported by a 4,000 gallon metalworking fluid system which used a DeLaval filtering system. Triazine was continuously fed into the system at the rate of four gallons per day. This system is referred to as D&I Line #1.

There were also two other D&I machining lines. These also operated on the same D&I platform as Line #1, and are referred to as Lines #2 and #3. Each of these lines had five machines. Lines #2 and #3 faced each other and were on one-half of the D&I platform, while Line #1 took up the other half of the platform. Lines #2 and #3 were supported by a 6,000 gallon sump which used a Schneider filter. Triazine was normally continuously fed into the system at the rate of six gallons per day. However, during this study no Triazine was added, since the plant chemist determined the system had an adequate level of biocide.

Two different employees from Line #1 and three employees from Line #3 wore silica-gel tubes which were changed at the middle of the shift, and dosimeters which were left on all day. Five different areas were also sampled around the sump and at the D&I platform. Background samples were taken on three employees and in one area. There were no samples taken during the addition of Triazine, since this was done continuously by a pump. Full shift average exposures were calculated based on morning and afternoon samples.

Again, due to a technical problem, there were no spiked samples taken in the field, but there were a number of duplicate samples taken.

Results

The results of all monitoring are shown in Tables I-III. The results of monitoring the metalworking coolant are shown in Table IV. Eight different control samples indicated background formaldehyde levels ranging from 34-74 ppb. The average of all of these values was 50 ppb, and the results were corrected by subtracting this value from all samples taken in the production facility.

A total of 31 personal air samples and 9 area air samples were taken during this survey. Twenty two of the 25 personal air samples taken in the D&I area exceeded 100 ppb and ranged from < 16- 282 ppb. If the background formaldehyde value of 50 ppb is subtracted from these results, 13 of the 25 samples still exceeded 100 ppb. Six of the seven area and source air samples taken at D&I and at the sump were above 100 ppb. Correcting for background reduces this to three of the seven area samples being above 100 ppb. In this facility, unlike the previous aluminum can facility, higher levels of formaldehyde were generally associated with metalworking fluid operations.

Samples taken on D&I workers with silica-gel tubes were separated into morning and afternoon samples, simply as a matter of increasing the number of individual data points. Time-weighted average results appear after the last sample and these can be compared directly to the dosimeter data which were obtained over the full shift. Two silica-gel tubes out of the twenty taken clearly had very low levels (23 and < 16 ppb). These were not calculated into the respective TWA calculation, since they were not believed to be representative of the actual exposures.

D&I operators on Line #3 had higher exposures to formaldehyde than the workers monitored on Line #2. This is consistent with the significantly higher levels of Triazine detected in the metalworking fluid system supplied to Lines #1 and #3. The two operations were physically close to each other, and one area (e.g. Lines #2 and #3) may have contributed to the exposure of the other (e.g. Line #1). Morning and afternoon samples were generally similar on all workers, and this is consistent with the stable levels of Triazine detected in the metalworking fluid.

Since spiked recovery samples were not taken in this survey, we again had the opportunity to examine precision among duplicate samples taken with the same type of monitor. The results of this comparison are shown in Table III. Neither method appeared to have worked as well as results found in the other aluminum can facility. Variability in the silica-gel tubes was mostly due to the two data pairs where there was very poor agreement due to low levels of formaldehyde reported in a single tube.

TABLE I
RESULTS OF FORMALDEHYDE MONITORING AT SITE #8

SAMPLE TYPE	OPERATION	DURATION (min)	FORMALDEHYDE CONCENTRATION (PPB) REPORTED VALUE	CORRECTED VALUE
Personal Air Samples				
Tube	D&I Operator #1, Line #1	216	121	71
Tube	(duplicate sample)	216	145	95
Tube	(repeat sample)	248	107	57
Tube	(duplicate sample)	248	123	73
Tube	TWA	464	123	73
Dosimeter	(duplicate sample)	464	98	48
Tube	D&I Operator #2, Line #1	201	167	117
Tube	(duplicate sample)	201	23	<22
Tube	(repeat sample)	233	162	112
Tube	(duplicate sample)	233	183	133
Tube	TWA	434	170	120
Dosimeter	(duplicate sample)	434	122	72
Tube	D&I Operator #1, Line #3	232	228	178
Tube	(duplicate sample)	232	224	174
Tube	(repeat sample)	226	192	142
Tube	(duplicate sample)	226	< 16	
Tube	TWA	458	209	159
Dosimeter	(duplicate sample)	458	147	97
Tube	D&I Operator #2, Line #3	188	152	102
Tube	(duplicate sample)	188	165	115
Tube	(repeat sample)	237	130	80
Tube	(duplicate sample)	237	160	110
Tube	TWA	425	151	101
Dosimeter	(duplicate sample)	425	134	84
Tube	D&I Operator #3, Line #3	177	282	232
Tube	(duplicate sample)	177	236	186
Tube	(repeat sample)	244	224	174
Tube	(duplicate sample)	244	214	164
Tube	TWA	421	235	185
Dosimeter	(duplicate sample)	421	148	98

<u>Area Air Samples</u>

Impinger	At Schneider Filter Press	374	71	<11
Dosimeter	(duplicate sample)	374	126	76
Impinger	At DeLaval Filter Press	377	151	101
Dosimeter	(duplicate sample)	377	162	112
Impinger	On D&I Platform	371	107	57
Dosimeter	On Operator's desk on D&I Platform between Lines #2 and #3	401	135	85
Dosimeter	On second level above D&I Operations	376	154	104

TABLE II
RESULTS OF FORMALDEHYDE MONITORING AT SITE #8
CONTROL SAMPLES

TYPE	OPERATION	DURATION (MIN)	FORMALDEHYDE CONCENTRATION (PPB)
Personal Air Samples			
Dosimeter	Briquette Opr.	437	65
Dosimeter	(duplicate sample)	437	74
Dosimeter	Palletizer #1	425	66
Dosimeter	(duplicate sample)	425	42
Dosimeter	Palletizer #2	418	66
Dosimeter	(duplicate sample)	418	42
Area Air Samples			
Dosimeter	On ground floor in general vicinity of palletizing operation	371	35
Dosimeter	(duplicate sample)	371	34

TABLE III
RESULTS OF FORMALDEHYDE MONITORING AT SITE #8
COMPARISON OF DUPLICATE SAMPLES-IDENTICAL MONITORS

TYPE	PERSONAL/AREA	RESULTS (PPB)	% DIFFERENCE
Tube	P	121, 145	7
Tube	P	107, 123	13
Tube	P	167, 23	86
Tube	P	162, 183	11
Tube	P	224, 228	2
Tube	P	<16, 192	96
Tube	P	152, 165	8
Tube	P	130, 160	9
Tube	P	282, 236	14
Tube	P	224, 214	4
Tube	P	282, 236	14
Summary: average difference= 24%, s.d. = 32, n=11			
Dosimeter	A	71, 126	44
Dosimeter	A	151, 162	7
Dosimeter	P	65, 74	12
Dosimeter	A	66, 42	36
Dosimeter	P	43, 40	7
Dosimeter	A	34, 35	3
Summary: average difference= 18%, s.d. =16, n=6			

TABLE IV
SUMMARY OF ANALYSES OF COOLANT SAMPLES AT SITE #8

SYSTEM	pH	TRIAZINE (PPM)
Line #1		
Morning Sample	8.74	1007
Afternoon Sample	8.74	944
Line #2		
Morning Sample	8.80	1828
Afternoon Sample	8.80	1818

SUMMARY OF FORMALDEHYDE EXPOSURE DATA

Background

Approximately 550 air samples were taken during this survey, and nearly 300 of these were obtained from workers. Every one of the nearly 300 personal air samples were below 500 ppb, 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.

A total of 16 air samples were taken at five different sites, while employees added concentrated Triazine to metalworking fluid systems. Each of these samples indicated non-detectable levels of formaldehyde, well below the OSHA Short-Term Exposure Limit of 2 ppm. Potential employee exposures during the addition of Triazine are not discussed in any further detail, due to the lack of any measurable exposure to formaldehyde.

Many of the air samples taken throughout this survey were below the LOQ. The values for these samples reflect the volume of air sampled. In other words, two samples which are reported as < 50 ppb and < 25 ppb, maybe similar and the difference may be due only to the volume of air sampled in each case. Several studies have recommended that one-half the limit of detection be used when performing statistical analyses on such samples. However, these studies only recommend this approach when a relatively small percentage of all samples are below the limit of detection (or LOQ for this study). Therefore, there was purposely an effort not to try to assign numerical values to samples which were below the LOQ, except as noted below.

Summary of Personal Air Sampling Data

The simplest and most statistically justified approach is to examine those samples above and below 100 ppb. Given that none of the time-weighted average personal air samples taken were above 500 ppb, 100 ppb is the next and only threshold for regulatory decision making using these data. All long-term air samples taken had a maximum LOQ below 100 ppb. Therefore, it is possible to discuss the data in terms of whether values were above or below 100 ppb, and the percentage of such samples.

The percentages of air samples taken on employees above and below 100 ppb are shown in Figure 1. Examining only data that were not corrected for background levels or recoveries of spiked samples, nine of the 12 operations monitored had at least one personal sample above 100 ppb. Six of the 12 operations had the majority of exposures monitored above 100 ppb.

The same data corrected for background levels and recoveries are shown in Figure 2. Eight of the 12 different operations monitored had at least one personal air sample above 100 ppb. Only two operations had a majority of samples above 100 ppb, and eight operations had the majority of samples below 100 ppb.

Summary of Area Air Samples

Approximately 250 air samples were taken at various operations where employees normally worked or at sources where high formaldehyde levels were anticipated. While employees took breaks from work, these samples remained at the location the entire sampling time. It was expected that these samples would demonstrate where the highest exposures were occurring and generally would have higher formaldehyde results than corresponding personal air samples. The results throughout this survey indicated area air samples to be lower than values obtained from employees, with the exception of those samples taken directly at metalworking fluid sumps. These samples are summarized in Figure 3. It can be seen that the majority of air samples taken at ten of the 12 operations were below 100 ppb, and that five of the locations had no sample above 100 ppb. These results are even more dramatic when corrected for background and spiked recoveries, as seen in Figure 4. Only one operation had the majority of area air samples above 100 ppb and eight of the 12 operations had ten percent or fewer samples above 100 ppb.

Collectively, the area sampling results indicate that Triazine-containing metalworking fluids are not producing levels of formaldehyde which are likely to cause exposures above the 100 ppb level 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.

Relationship Between Triazine Levels and Formaldehyde Exposures

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. Figure 5 illustrates the percentage of personal air samples above 100 ppb and whether this percentage increased or decreased after the addition of Triazine. Only corrected data were used, since high background levels or poor spiked recoveries might mask the affects of Triazine addition on formaldehyde exposures. The data shown in Figure 5 indicate that for ten operations; the percentage of exposures above 100 ppb remained the same at six, exposures increased at three operations and exposures decreased at one operation.

Individual data points were plotted by ppb-formaldehyde based on whether samples were taken before or after the addition of

Triazine. Because of difficulty noted before with samples below the LOQ, only paired samples were used when obtained with the same sampling device and when at least one of the two samples had a detectable quantity of formaldehyde (any samples less than the LOQ were recorded as half the value). The results shown in Figure 6 indicates that there was not a statistically significant relationship between the exposure levels obtained before the addition of Triazine and those after the addition. The regression line plotted indicates that exposures after the addition of Triazine were generally higher than samples taken before the addition of Triazine. Two high data points (above 150 ppb formaldehyde before Triazine was added) were excluded from this analyses, as these two points tended to bias the results (the resultant coefficient of correlation went from 0.30 to 0.54).

This relationship is important in determining a cause and effect between Triazine levels in metalworking fluid and formaldehyde exposures. One problem with this analysis was the tremendous variability in differences between the concentrations of Triazine in the metalworking fluids before and after additions.

<u>Predicting Formaldehyde Exposures Based on Triazine Levels</u>

Another way to examine the effects of Triazine on formaldehyde exposures is to examine whether there is an effect between the concentration of Triazine in metalworking fluid and the percentage of exposures greater than 100 ppb. The percentages of exposures above 100 ppb were calculated for each operation (except Site #1) for both morning (pre-treatment) and afternoon (post-treatment) exposures. These values were then plotted against the concentration (in ppm) of Triazine in the metalworking fluid. The results of this analysis are shown in Figure 7. There is a weak, but statistically significant relationship between Triazine levels in metalworking fluid and the percentages of exposures above 100 ppb.

The data in Figure 7 were further analyzed by examining only the data obtained in the morning. The reason for this is that an equilibrium between formaldehyde levels in the air and Triazine concentration in metalworking fluid probably existed in the morning. It is likely that this equilibrium was disrupted when Triazine was added to the fluid. In fact, one of the premises of the study was that after the addition of Triazine, exposures are likely to represent employees' highest exposures to formaldehyde. The data from only the morning are shown in Figure 8. Here the relationship becomes much stronger and more predictive. These data suggest that one can predict formaldehyde levels based on Triazine concentrations in metalworking fluids.

It is not clear from the OSHA regulation what percentage of employee exposures above 100 ppb is allowable before labelling and training requirements of the formaldehyde standard are required.

If the answer is none, then Triazine levels must be kept below 250 ppm in metalworking fluid to begin to reach this goal. Unfortunately, at this level Triazine will not be an effective biocide. If for example the answer is a majority of exposures (50%) must be below 100 ppb, then the current labelling indicating a maximum use concentration of 1500 ppm is appropriate.

Effect of pH on Formaldehyde Exposures

The other variable measured in this study was the pH of the metalworking fluid. A similar set of analyses as was performed on Triazine levels was done with pH, and the results can be seen in Figures 9 and 10. Unlike with Triazine concentrations, there is no relationship at all between pH and formaldehyde exposures over the ranges measured in this study. This does not suggest that pH will not be a factor, but simply that for the range measured in this study, pH was not significant.

Comparison of Different Sampling Methods

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. None of the data for short-term sampling, which generally indicated values below the LOQ, were used in this analyses. Where data were listed as below the LOQ, half the LOQ value was used for these analyses. A comparison of data with dosimeters and silica-gel tubes is shown in Figure 11. Although there is a statistically significant relationship, many data points indicate significant differences between the two methods. Overall, the average silica-gel tube results were nearly twice (1.87) the value obtained with dosimeters. The data plotted with impingers and dosimeters is shown in Figure 12. The results indicate that there is no relationship between data obtained with dosimeters and impingers. A much smaller data set is available for impingers and silica-gel tubes and is shown in Figure 13. Again, there is no statistically significant relationship. However, the analyses is greatly affected by two extreme data points taken at or above 1000 ppb. If these data points are excluded from the analyses, the results are shown in Figure 14. The relationship between impingers and silica-gel tubes have a high coefficient of correlation (0.86) and are statistically significant. The slope of this line is 0.4, meaning that silica-gel tube results are on average about two and a half times greater than values obtained with impingers.

In summary, the highest results from this survey were obtained with silica-gel tubes. There was a good agreement between results obtained with silica-gel tubes and impingers and a poorer agreement between dosimeters and silica-gel tubes. There was no relationship from results obtained between dosimeters and impingers.

Precision Among Sampling Methods

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 over this study. Each pair of points were analyzed by calculating the difference between pairs as a percentage of the larger sample. Again, where LOQ samples existed, one-half the LOQ value was used. None of the short-term samples were considered in this analyses, since they almost all had values below the LOQ.

A summary of the results can be seen in Table I and Figure 15. The data suggests that dosimeters and impingers have the greatest percentage of duplicate samples which varied by less than ten percent. It should be noted that the data set for impingers (four duplicate pairs) was very limited. 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. An alternate method of examining the variability of duplicate samples is to use the mean difference plus or minus two standard deviations (95% confidence level for normal distribution of variability). Using this approach, 95% of all dosimeter values should be within 47% of each other and for silica gel tubes this value is 83%.

The time-weighted average personal air sampling data, shown in Figure 2, was recalculated using this information. The data is now shown in Figure 16 with percentage above 100 ppb, below 100 ppb and with percentages showing uncertainty due to variability in the precision of each method. For dosimeters, results below 50 ppb are considered to be below 100 ppb, and results above 150 ppb to be above 100 ppb. Results between 50 and 150 ppb are considered uncertain as to whether values exceed or do not exceed this limit. The same approach is shown for silica-gel tubes, only the cut-off points are 35 and 165 ppb.

Comparing the results from Figures 2 and 16 indicate that many results now become uncertain. Using this analysis, the number of operations where an exposure above 100 ppb was found goes from eight out of 12, to only five of 12. There are no operations where more than approximately 35% of the samples exceeded 100 ppb, where before four of the 12 facilities had 50% or more of the samples above 100 ppb.

Accuracy of Sampling Methods

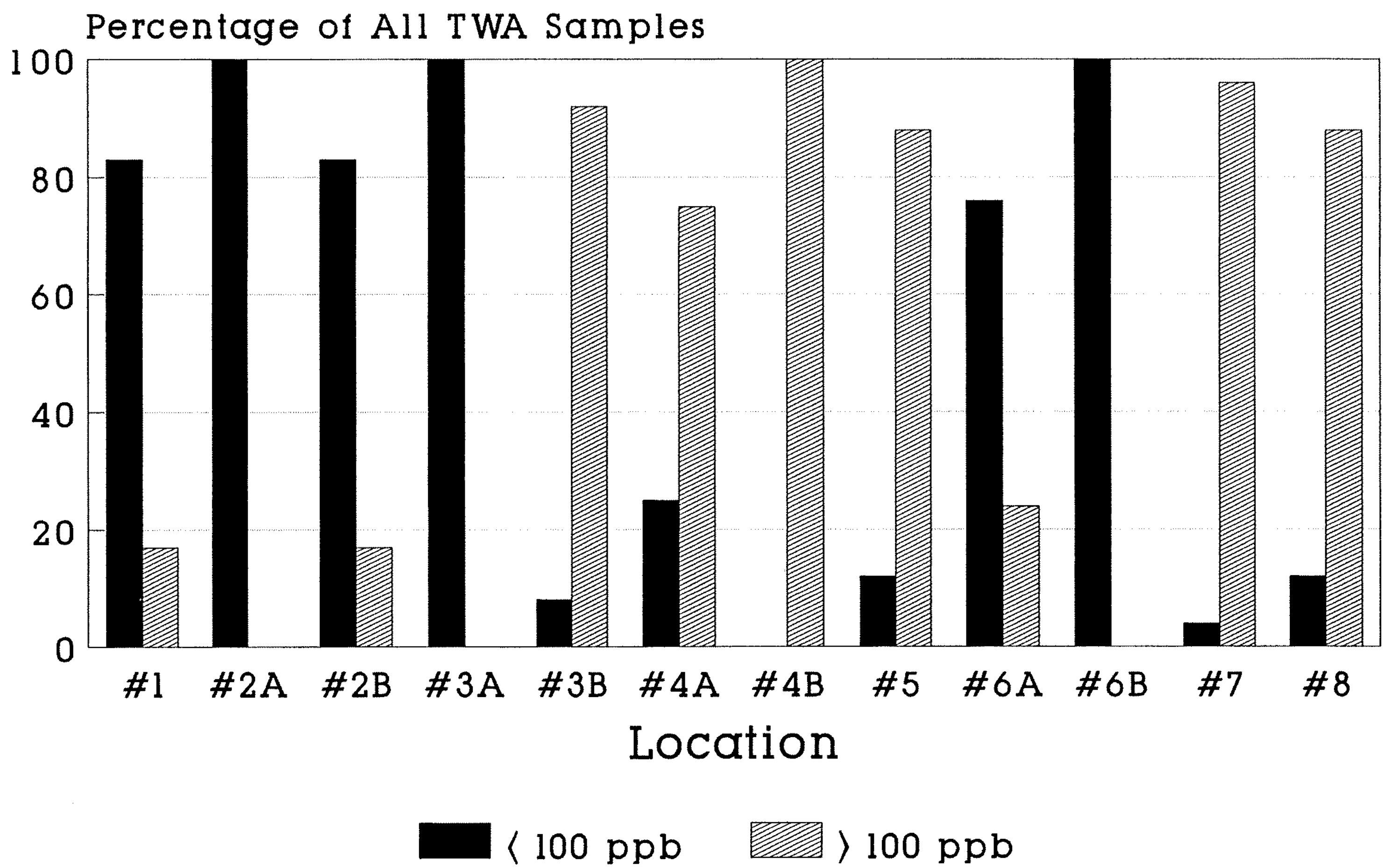
The accuracy of each of the sampling methods is a combination of the precision and bias for each method. Precision has been discussed above. Bias can be estimated by examining the ability of each method to recover spikes of formaldehyde. A summary of all recovered spiked values for all three methods is displayed in Table I. All three methods had a positive bias. The average bias was 10-22% for the three methods. The accuracy of each method is a combination of the precision and bias. The accuracy of the dosimeters was ± 32%, the silica-gel tubes were ± 35% and the impingers were ± 46%.

TABLE I
SUMMARY OF PRECISION AND ANALYSES OF SAMPLING METHODS

STATISTIC	DOSIMETER	SILICA-GEL TUBE	IMPINGER
Analyses of Duplicate Samples			
n =	22	26	4
Range =	0-77%	0-91%	0-51%
mean = (% difference between duplicate samples)	9.8	24.8	25.5
standard deviation=	18.8	29.2	25.5
precision at 95% confidence level (mean ± 2 standard deviations)	47.4%	83.2%	*
* = insufficient data			
Analyses of Recovery Data For Spiked Formaldehyde Samples			
n =	25*	46	20
range =	20-390%	50-197%	86-157%
mean = (% recovery)	122	110	121
standard deviation=	67	22	18

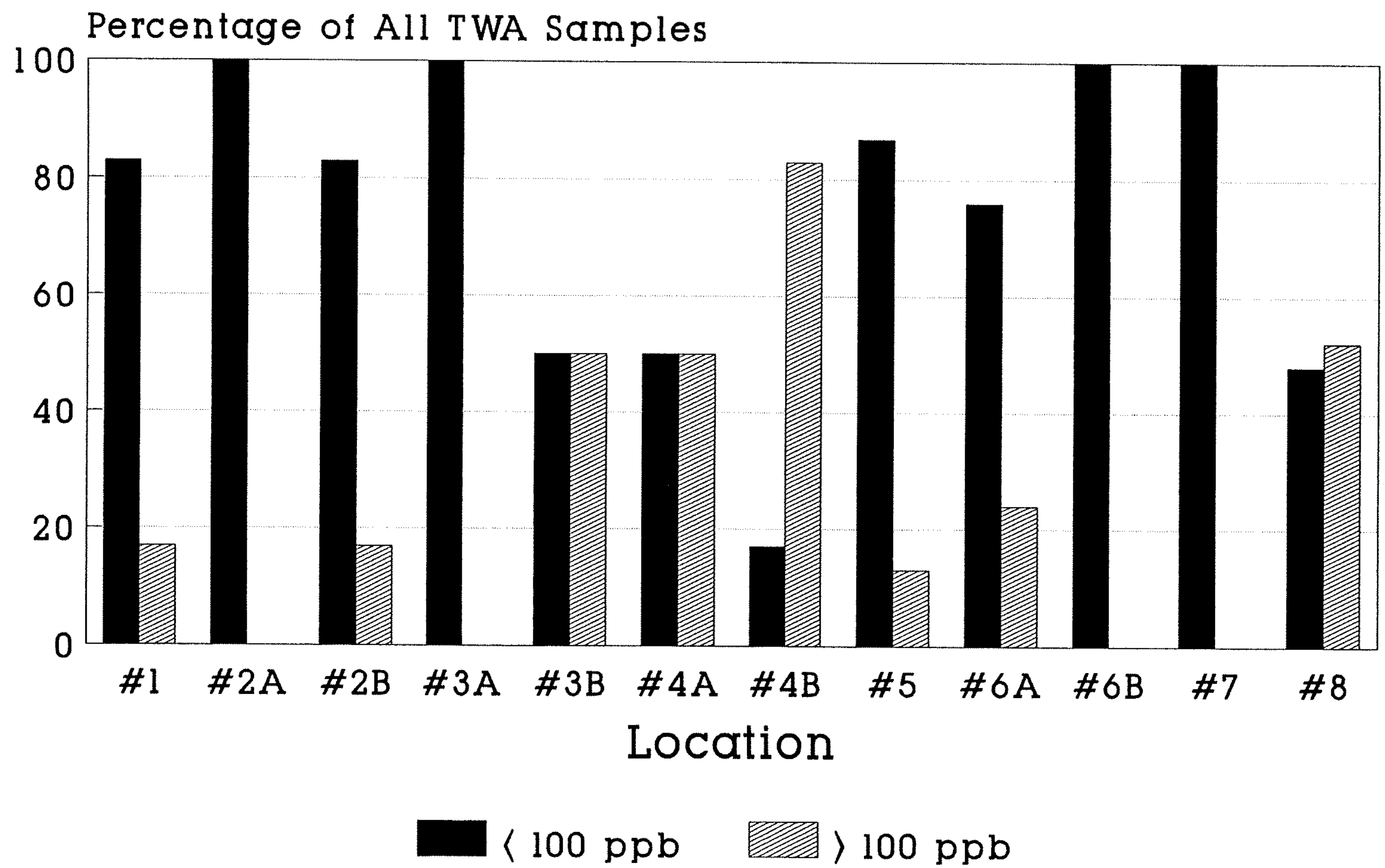
* = one outlier of 610% eliminated from analyses of dosimeter data.

FIGURE 1
SUMMARY OF PERSONAL AIR SAMPLING DATA



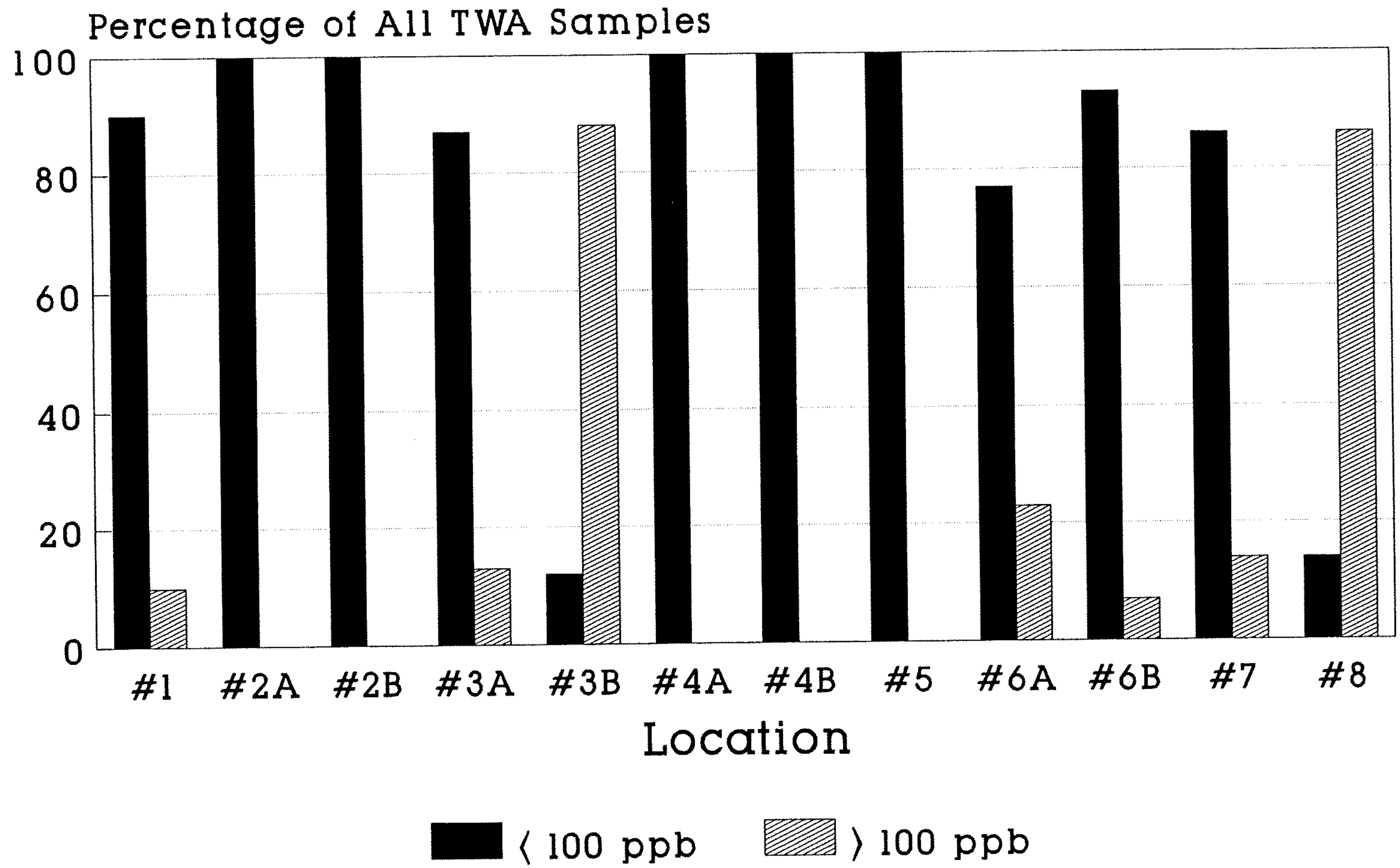
UNCORRECTED VALUES

FIGURE 2
SUMMARY OF PERSONAL AIR SAMPLING DATA



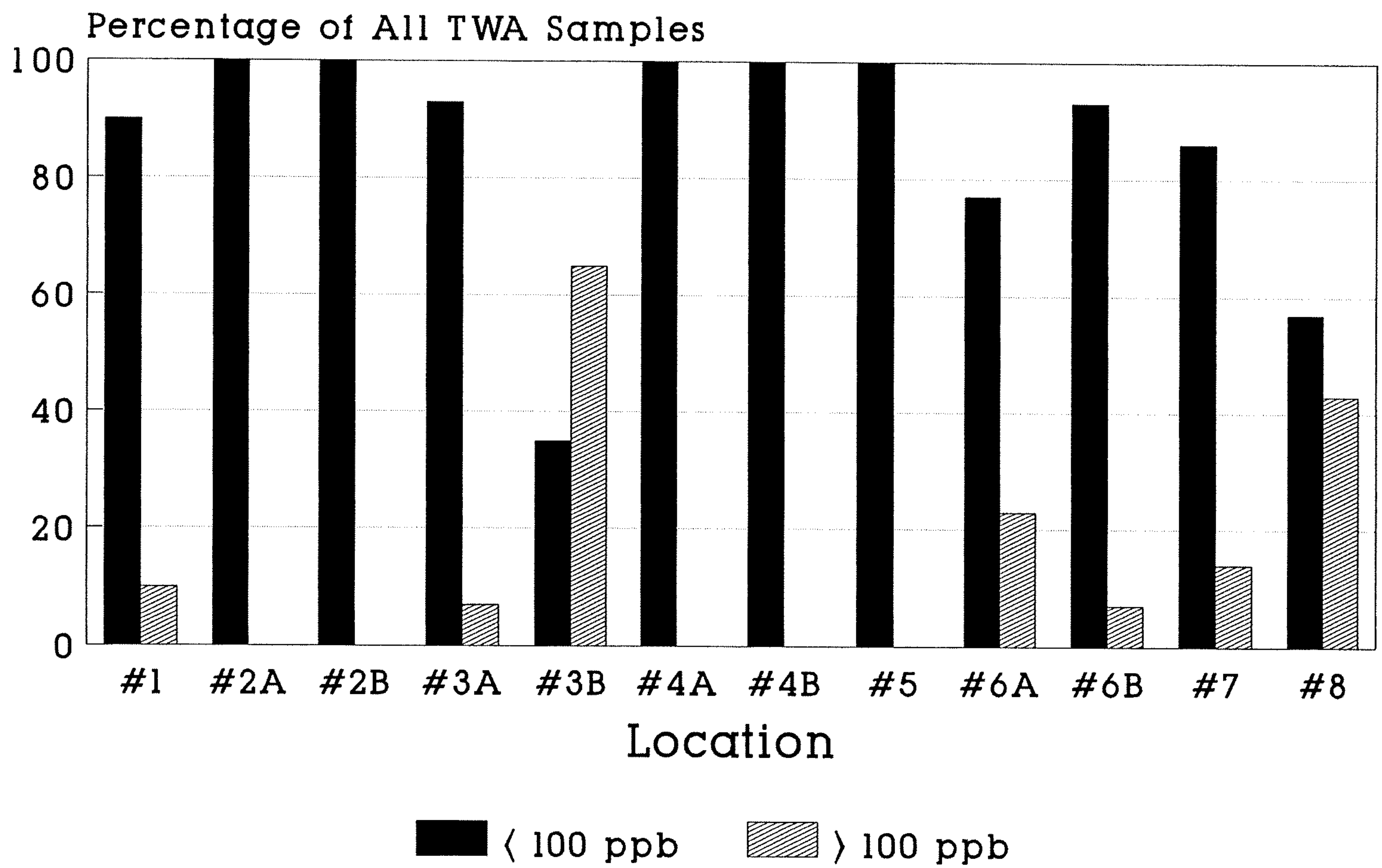
CORRECTED VALUES

FIGURE 3
SUMMARY OF AREA AIR SAMPLING DATA



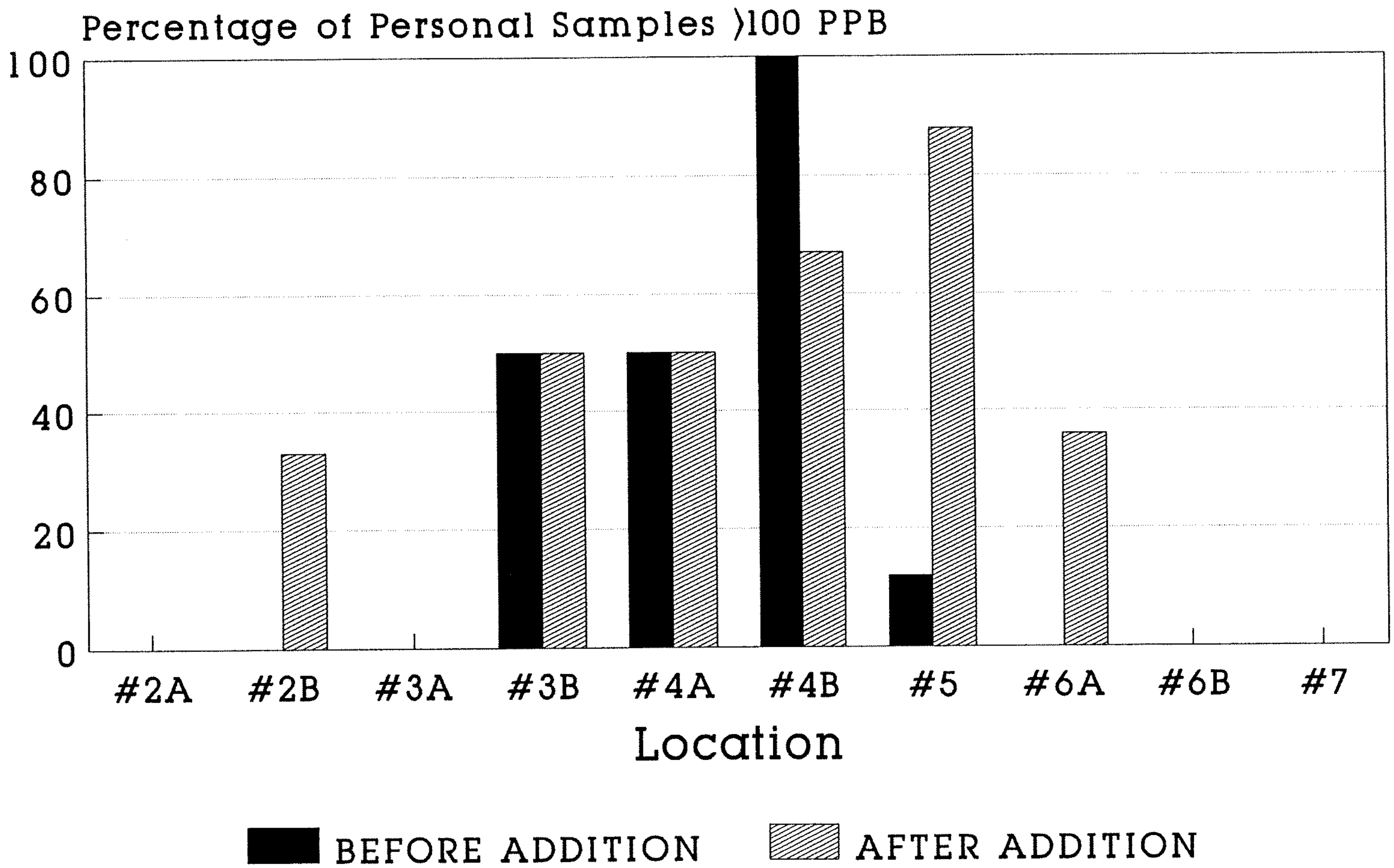
UNORRECTED VALUES

FIGURE 4
SUMMARY OF AREA AIR SAMPLING DATA



CORRECTED VALUES

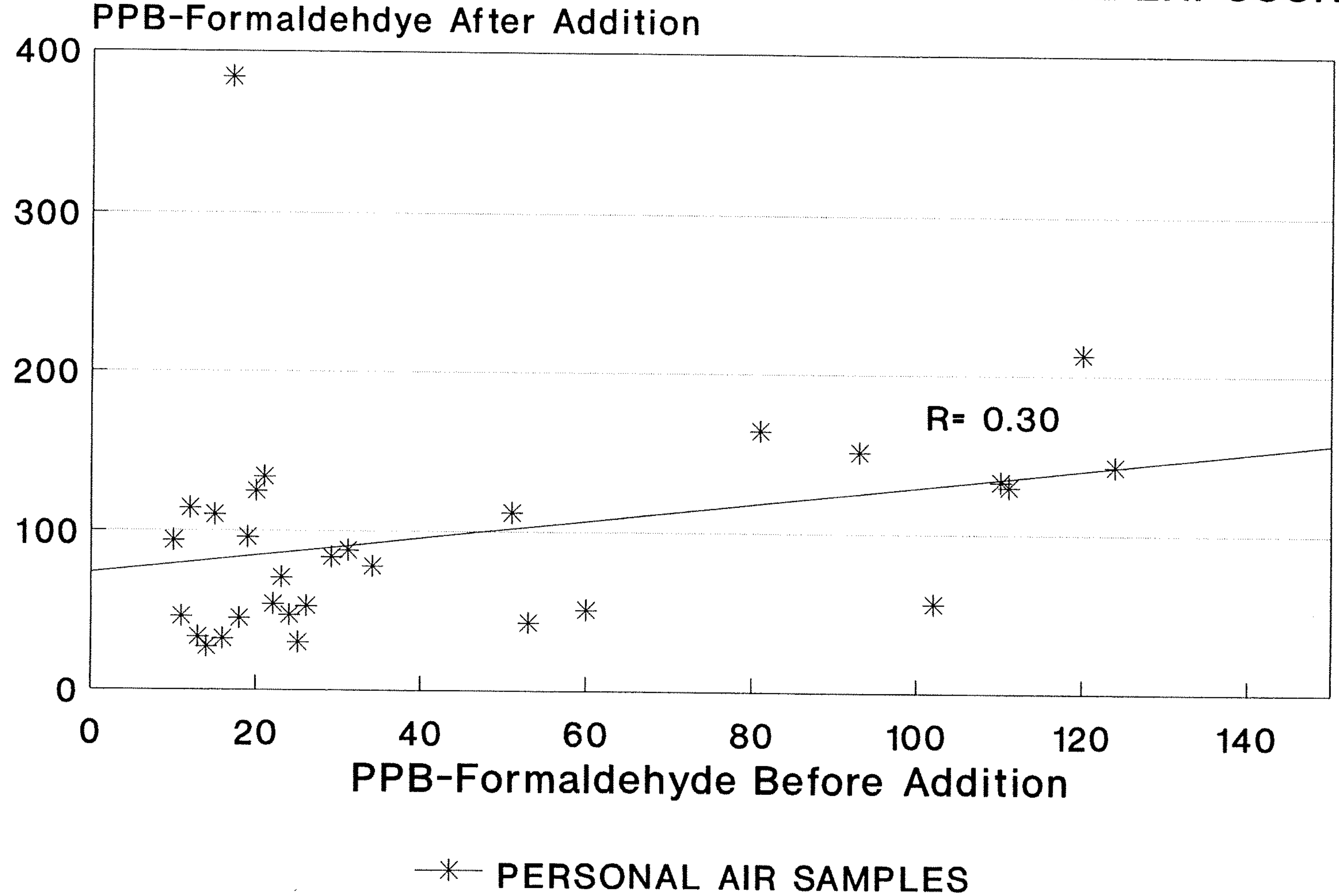
FIGURE 5
EFFECT OF TRIAZINE ADDITION



CORRECTED VALUES

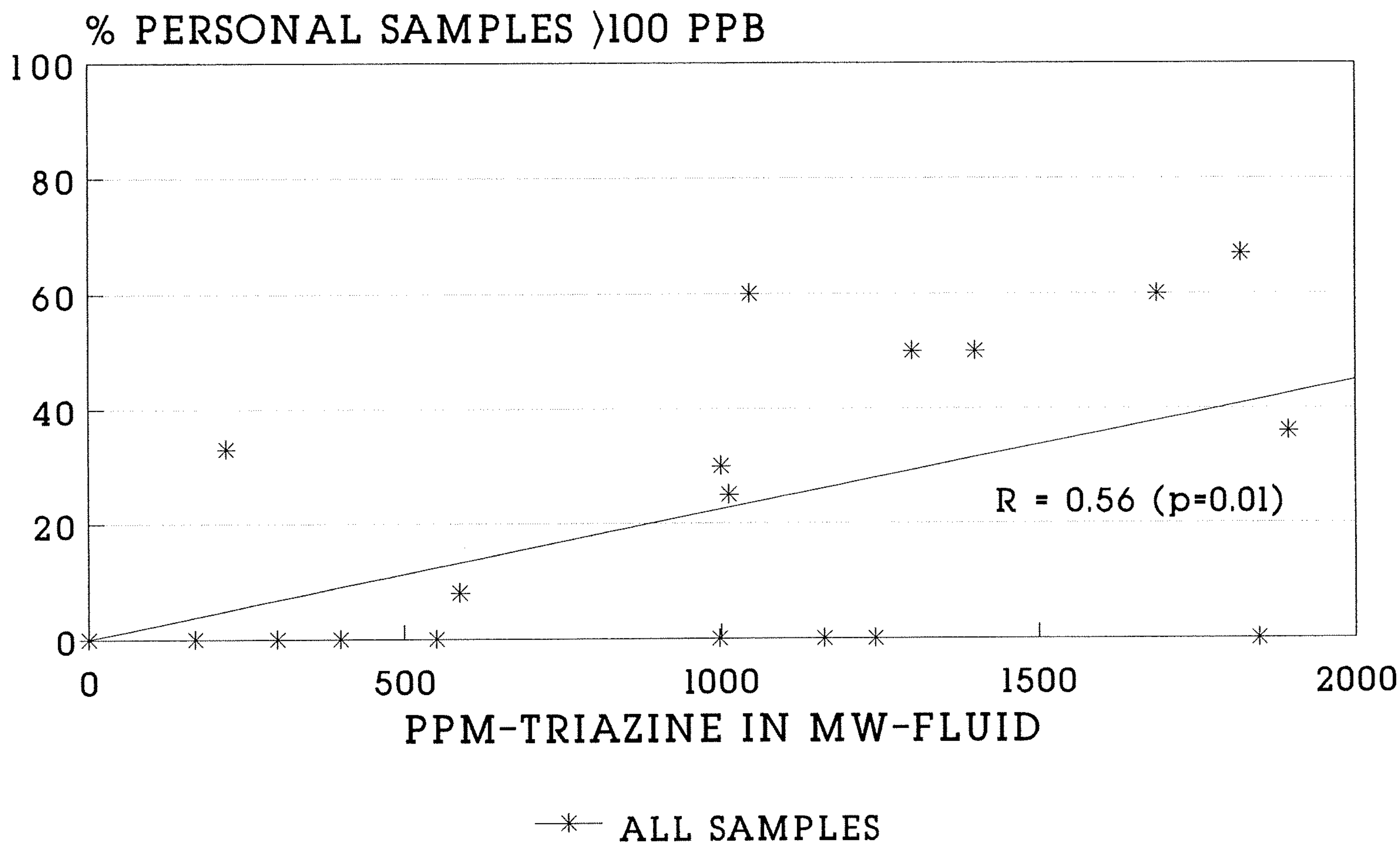
FIGURE 6

EFFECT OF TRIAZINE ADDITIONS ON FORMALDEHYDE EXPOSURES



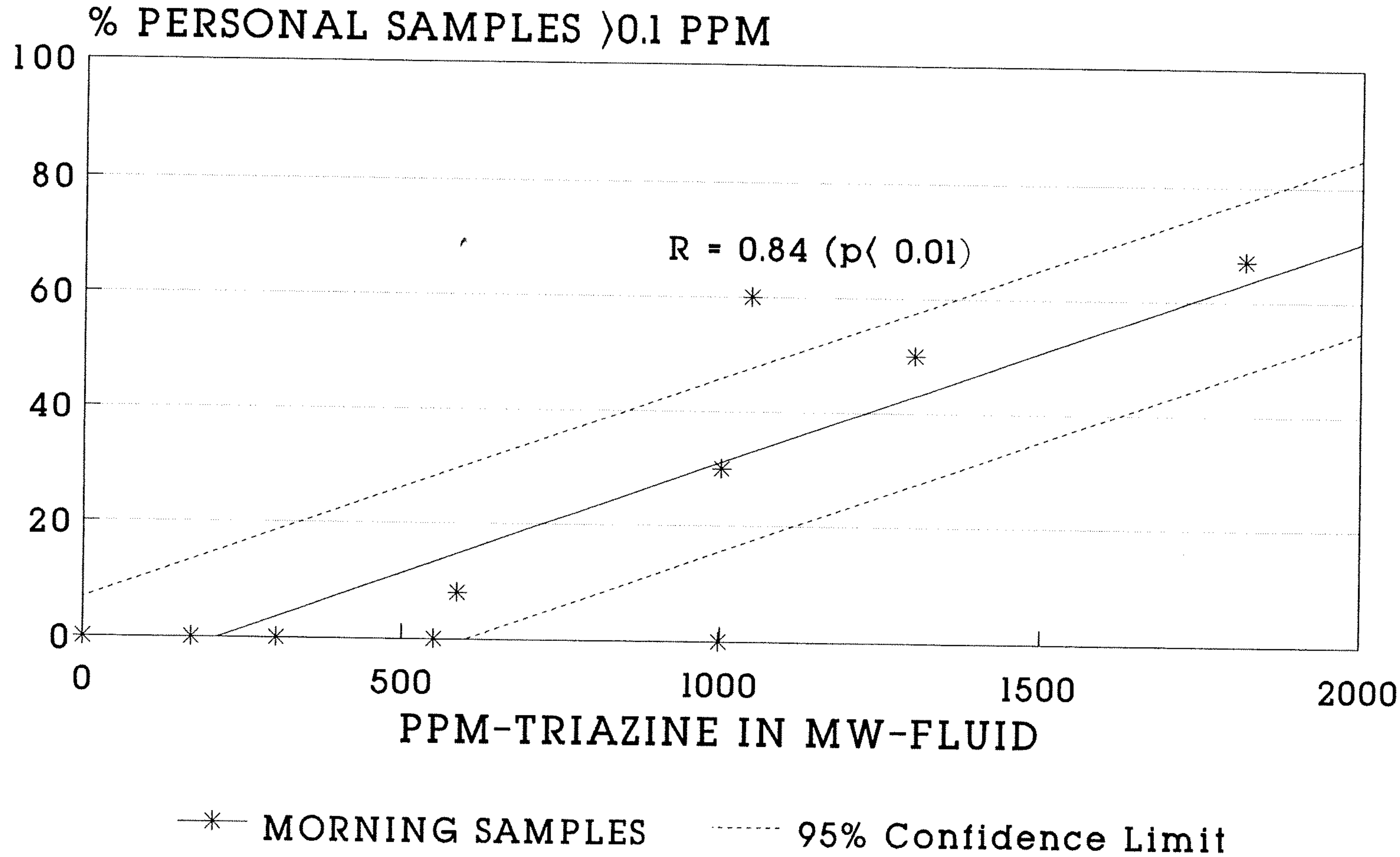
Corrected Values

FIGURE 7
EFFECT OF TRIAZINE ON EXPOSURE LEVELS



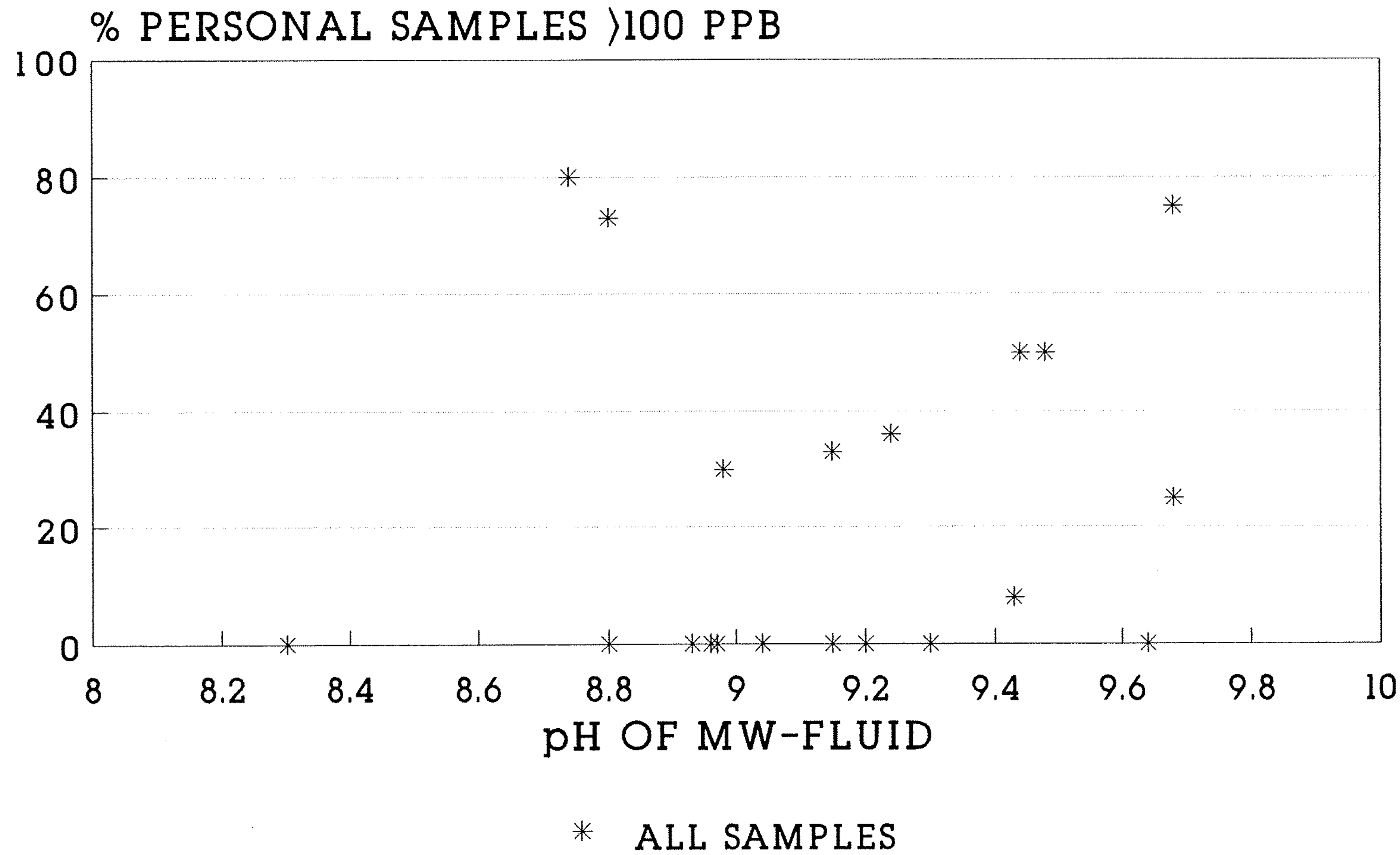
CORRECTED TWA SAMPLES

FIGURE 8
EFFECT OF TRIAZINE ON EXPOSURE LEVELS



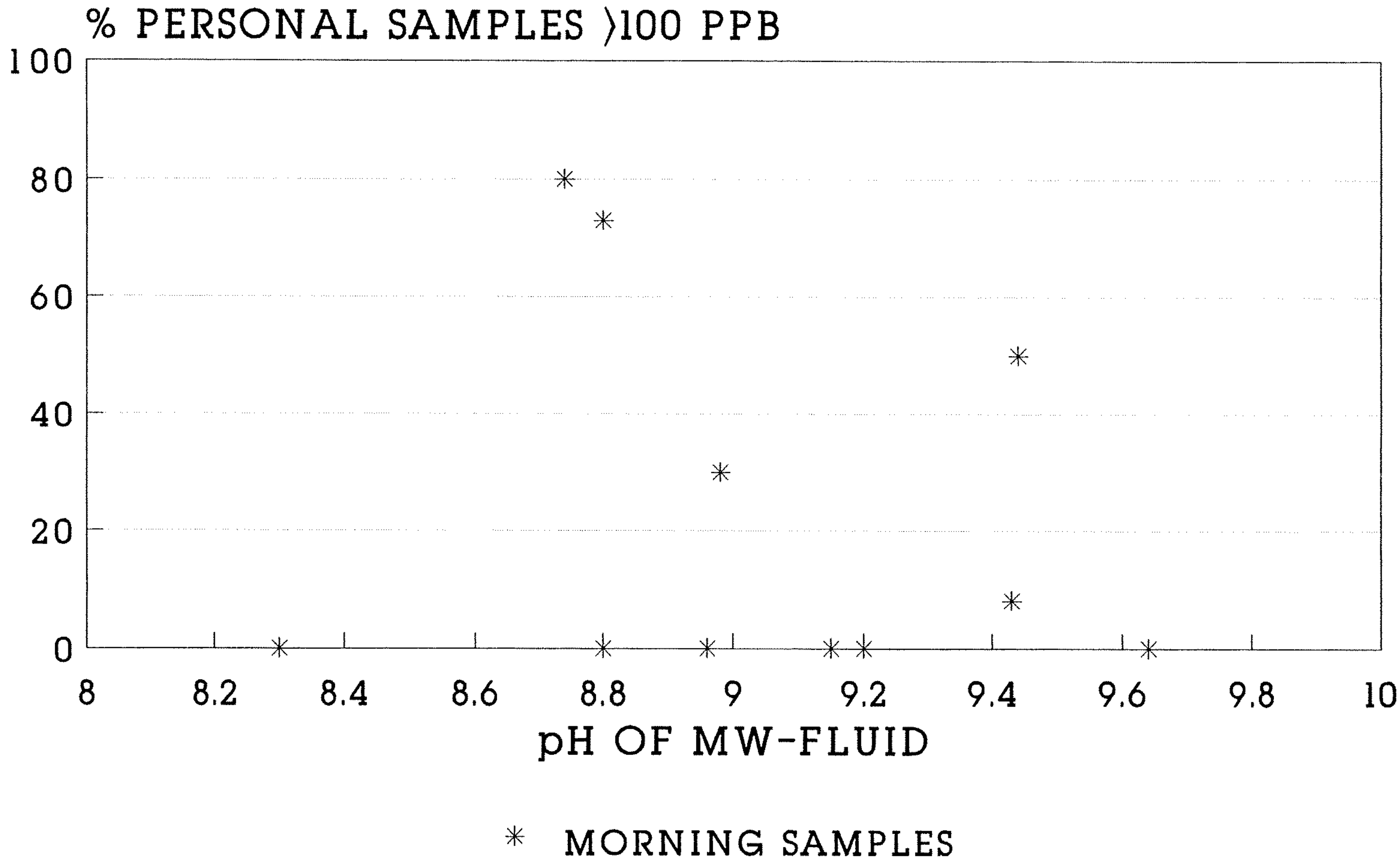
CORRECTED TWA SAMPLES

FIGURE 9
EFFECT OF pH ON EXPOSURE LEVELS



CORRECTED TWA SAMPLES

FIGURE 10
EFFECT OF pH ON EXPOSURE LEVELS



CORRECTED TWA SAMPLES

FIGURE 11
COMPARISON OF MONITORING METHODS

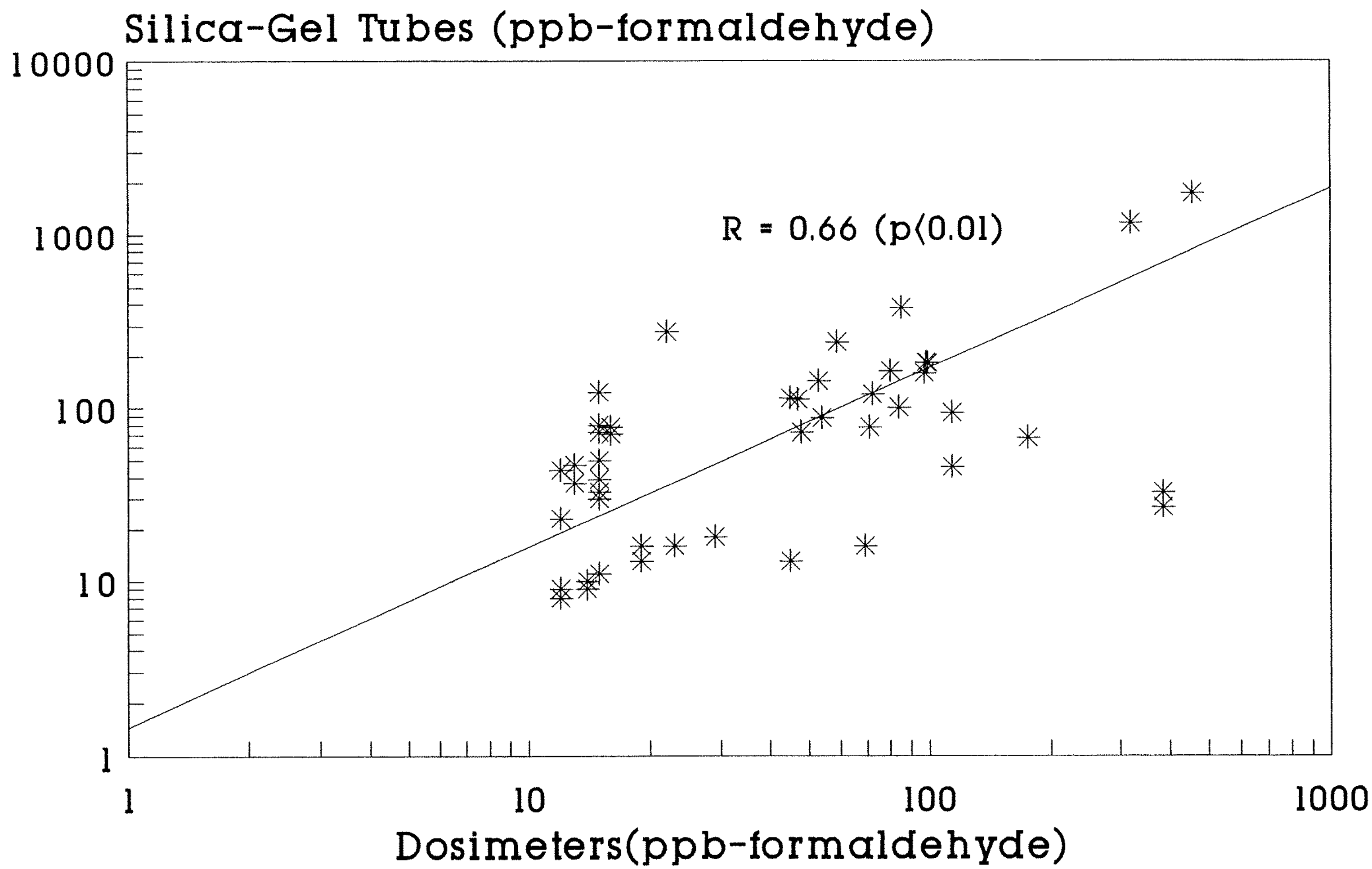


FIGURE 12
COMPARISON OF MONITORING METHODS

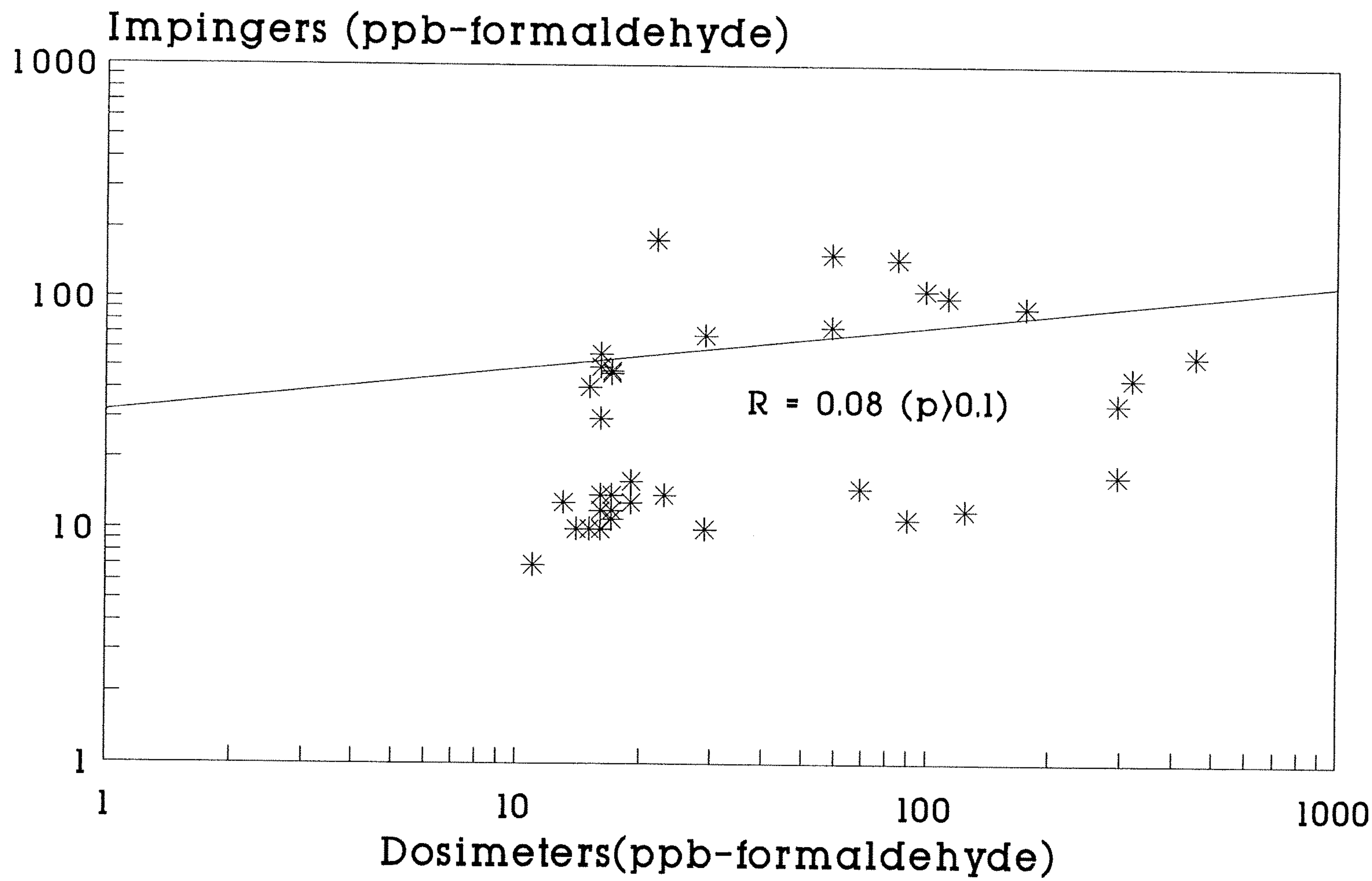


FIGURE 13
COMPARISON OF MONITORING METHODS

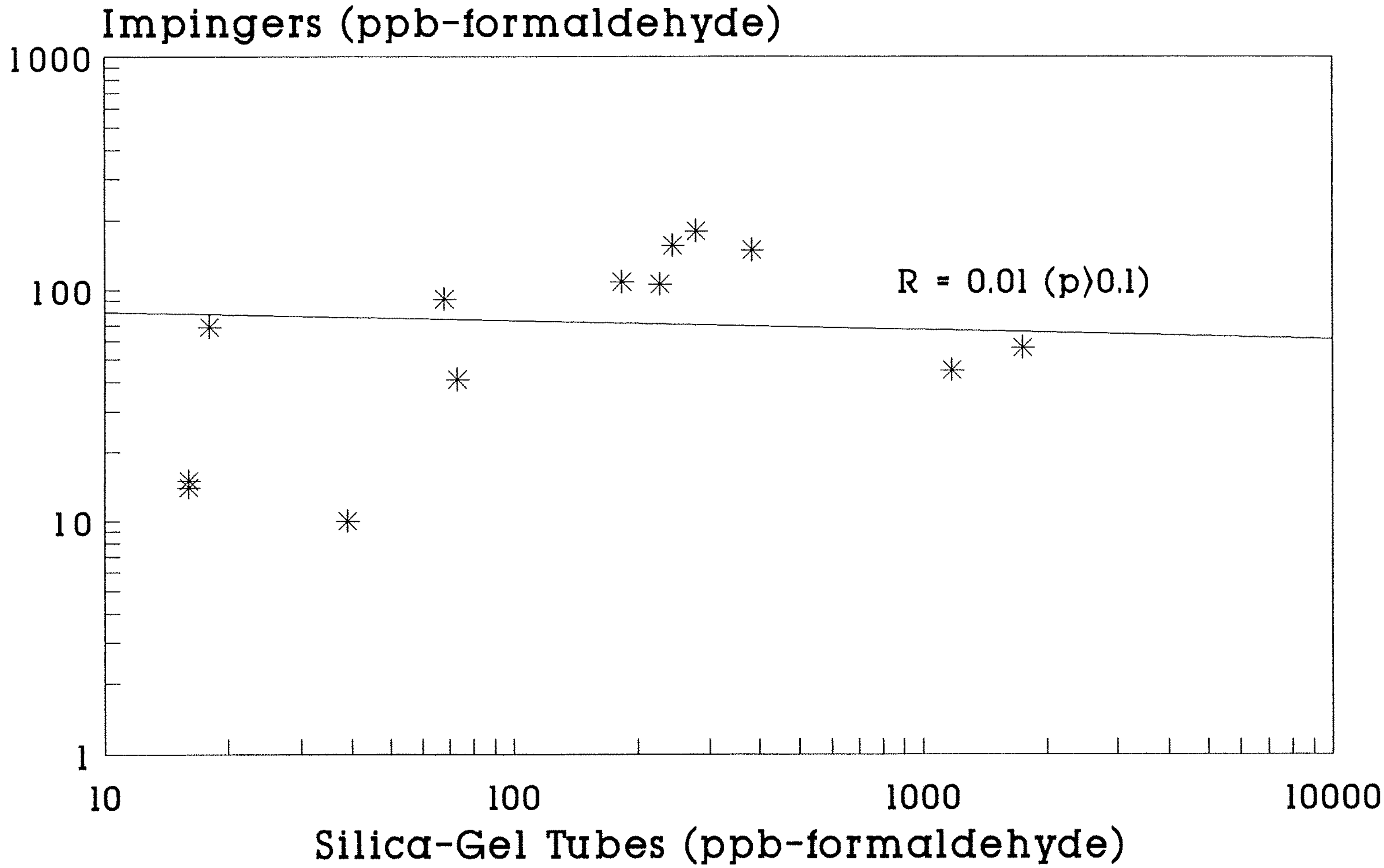


FIGURE 14
COMPARISON OF MONITORING METHODS

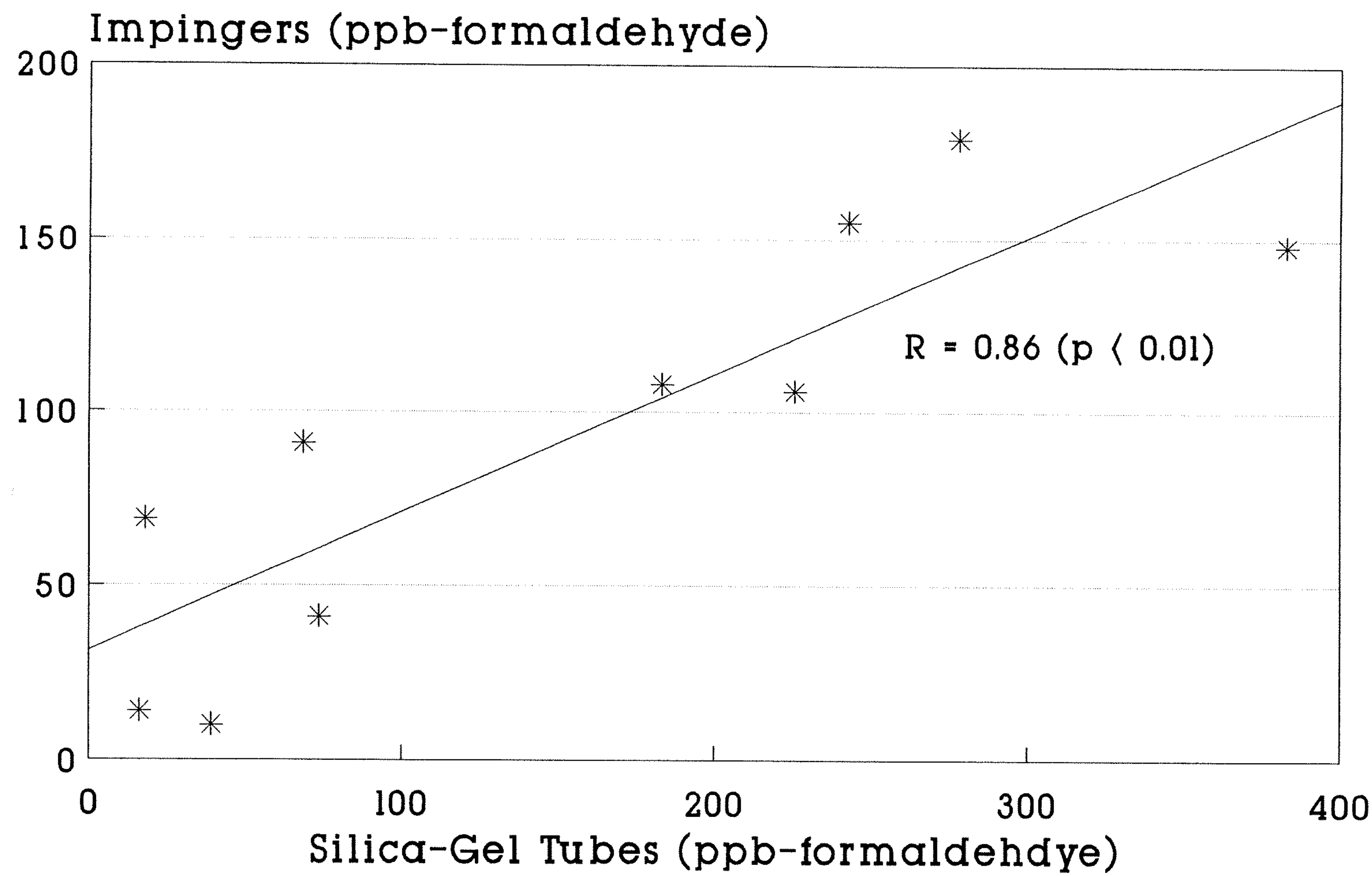


FIGURE 15
PRECISION OF REPLICATE SAMPLES

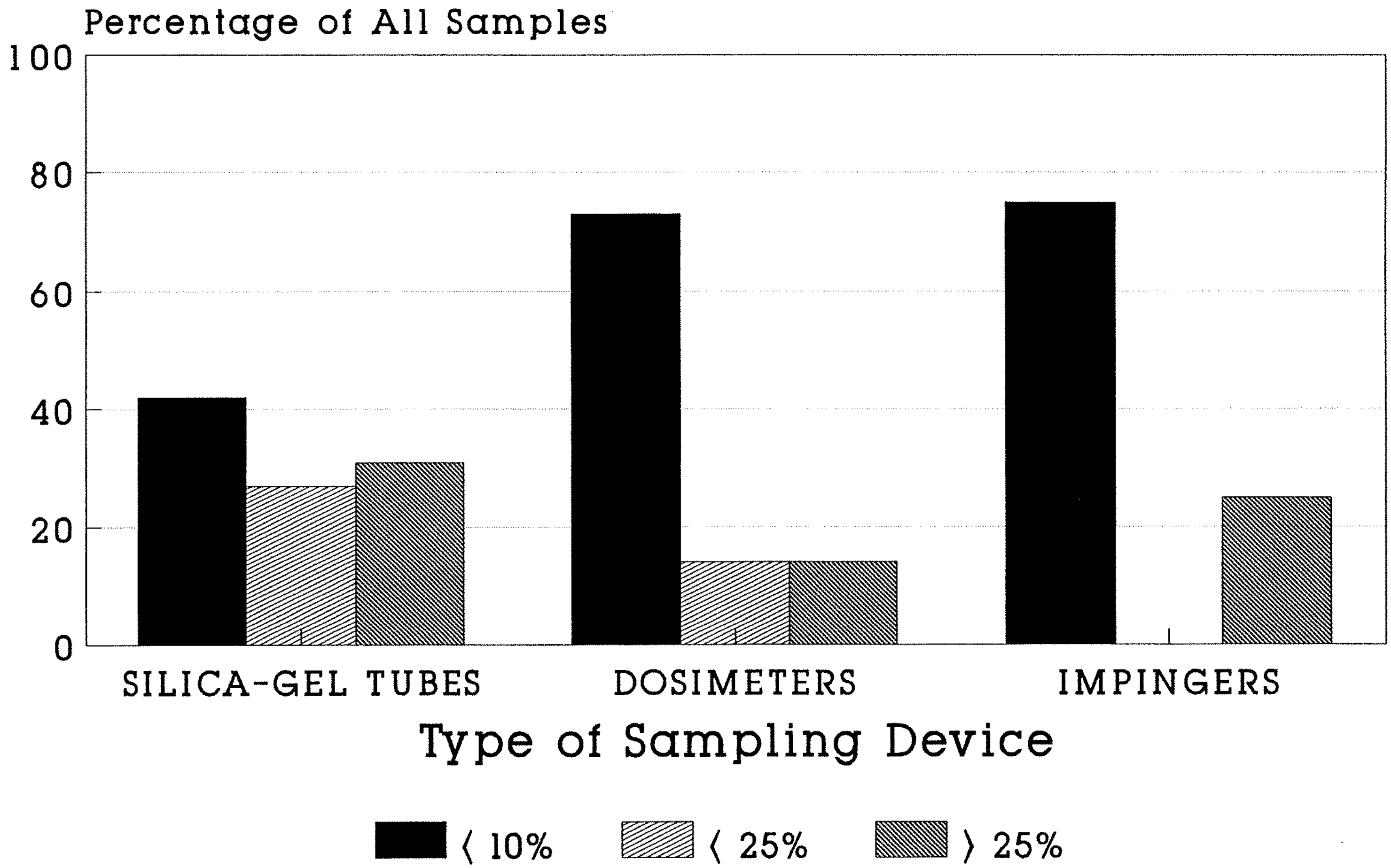
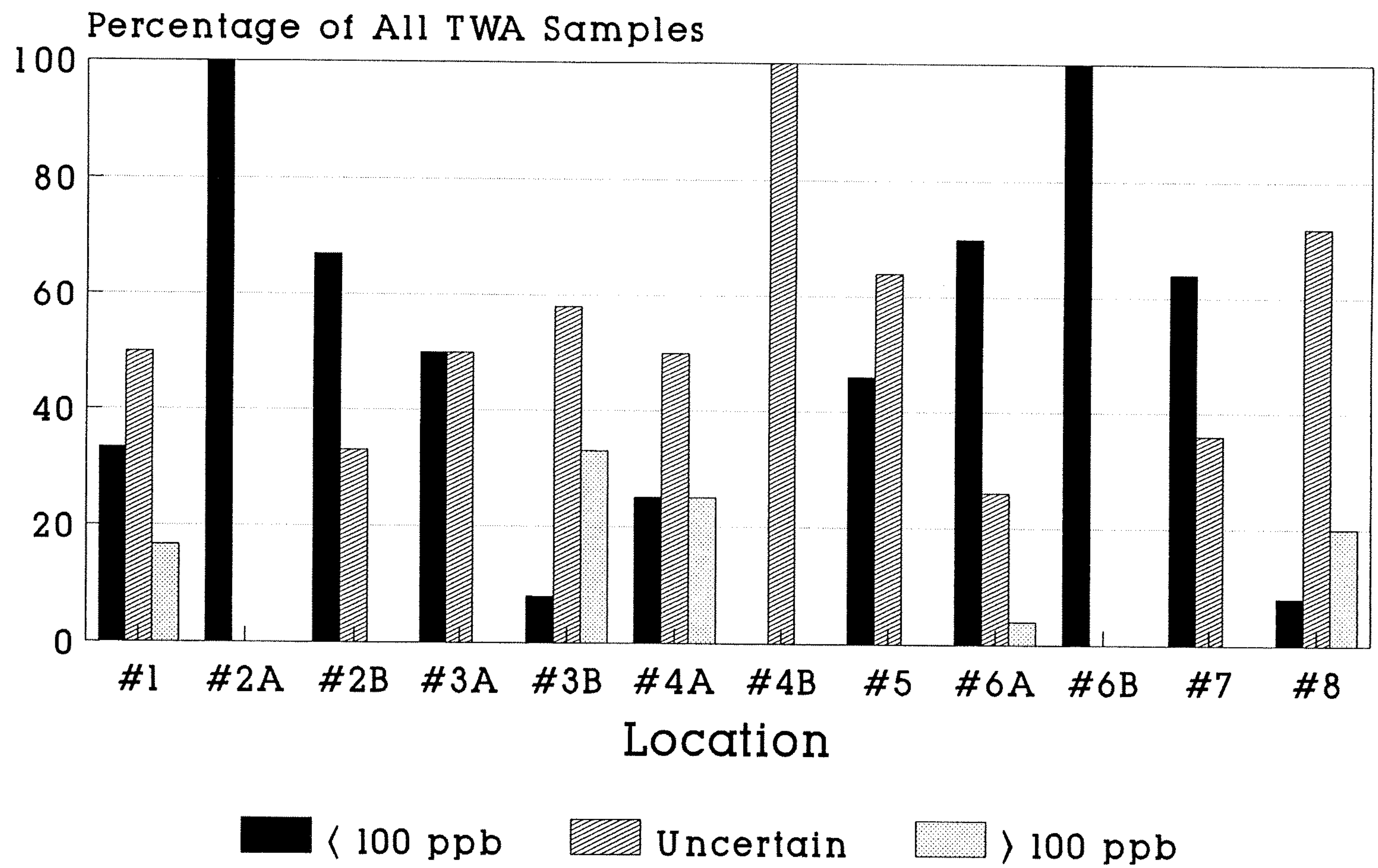


FIGURE 16
SUMMARY OF PERSONAL AIR SAMPLING DATA



CORRECTED VALUES

CONCLUSIONS

The purpose of this study was to document the range of formaldehyde exposures to employees using metalworking fluids containing Triazine. The results of this study indicate that employees involved in these operations will not be 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. The only exception could be employees who perform prolonged maintenance activities inside poorly ventilated sumps. The data contained in this report can be used by employers using Triazine biocides in metalworking fluids to avoid having to perform baseline exposure monitoring, as required by OSHA in the Formaldehyde Standard.

When this study was initiated it was unclear whether certain operations might be responsible for higher exposures to formaldehyde. Such operations could be grinding parts where metalworking fluid would be aerosolized in the workers' breathing zones or activities in which concentrated Triazine was handled (e.g. replenishing Triazine in sumps). One interesting finding was that employees working at a variety of different operations using the same metalworking fluid tended to have similar exposures regardless of their specific activity. A statistical evaluation of formaldehyde exposures confirmed that there was a predictive relationship with Triazine levels in metalworking fluids. The level of Triazine required to insure that no employee is exposed to above 0.1 ppm was approximately 250 ppm in solution. This level will not allow Triazine to be an effective biocide of metalworking fluid.

This is one of a few investigations which has attempted to quantitatively examine low levels of formaldehyde exposures. Since formaldehyde is ubiquitous in most environments, background levels can represent a significant percentage of the overall exposure when examining a threshold of 0.1 ppm. Several locations had measurable background levels of formaldehyde, and in one case these levels were higher than exposures associated with the use of Triazine. Data were corrected in this study so that exposures due to the use of Triazine, and not other products, could be examined. Another problem encountered with examining low levels of formaldehyde concerned using established sampling and analytical methods. Although existing methods have the capability of detecting formaldehyde levels below 0.1 ppm, their accuracy and precision had not been validated at these levels. This study found significant variability with the precision of these methods and a generally positive bias of ten to 20 percent.

Some employee exposures to formaldehyde above 0.1 ppm were observed related to the use of Triazine, even when considering the imprecision and bias of the sampling methods, and correcting for background levels of formaldehyde. The OSHA Formaldehyde standard does not indicate a specific percentage of employee exposures above 0.1 ppm necessary before compliance with the labelling and training specifications is required. Unless employers have their own exposure data indicating formaldehyde levels below 0.1 ppm, a conservative approach would suggest that existing hazard communication training incorporate information on the hazards of formaldehyde and possible exposures from sumps with metalworking fluids containing Triazine.