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Solvent Exposure during use of Solvent-Based Whiteboard Markers

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Introduction

Whiteboards have, for the most part, replaced the traditional chalk board in the classroom setting. Potential for exposures to individual users has been investigated. For one user, even with heavy use, the maximum solvent exposure measured is <2 ppm of solvent. CPSC has recently been contacted by school systems that describe a new use of these markers. Whiteboards are cut up into small sections and distributed to students in a classroom. Each student then uses the boards and whiteboard markers for a class project. CPSC, in cooperation with Duke, reviewed the generic formulas, by class, for all whiteboard markers certified by the Art & Creative Materials Institute (ACMI). Whiteboard marker inks have solvent systems that may contain water, alcohol , various glycols, ketones or acetates. CPSC expressed concern over the possibility of overexposures to highly volatile ketone and acetate solvents. Based on their concern the following study was designed to address whether or not use of whiteboard markers by many students at once may create an overexposure situation.

Study Design

Four (4) different colored markers were used by participants to color whiteboards while working within 2 meters of each participant in each study. One series of studies, using 1,3 or 5 participants, was conducted in a room with little air infiltration (double glass insulated windows, an exterior, floor vapor barrier) and no recirculation and a room volume of 230 m^3. A comparative series of studies, involving 1,2 or 4 participants, was conducted with the same colored markers in a schoolroom with a volume of 237 m^3 with a re-circulating, room-specific, HAC system that was on during experiments resulting in noticeable air movement. Participants worked on tables arranged around a 2 meter diameter circle. Whiteboard material was obtained and cut into 24" x 33" pieces for use by each participant. Participants drew on whiteboards for 30 minutes.

Markers using a solvent system based on methyl isobutyl ketone and n-butyl acetate were chosen for this study. In order to limit variability from one user to the next and to conserve resources, only 4 colors of marker ink were used in this study. Each marker was weighed to the nearest 0.1 mg before and after each test to determine ink consumption. Solvent consumption was determined by multiplying the ink consumption by the percentage of each solvent present in the mixing formula for each color.

Solvent exposures were determined by sampling in the breathing zone of users and at a distance of 4 m from the work area at a height of 2 m (background (area) sampling). Total sampling time was 4 hours for each trial. Breathing zone samplers were moved to the background sampler site for the last

3 ½ hours of sampling for each trial.

Air sampling was done with a passive diffusion monitor (3M, Model 3500). At the end of each run, samplers were sealed and refrigerated. They were then shipped overnight for analysis by a certified industrial hygiene laboratory (B.I.C., Minneapolis, MN). Analysis is done by carbon disulfide desorption followed by analysis by gas chromatography with correction for both relative humidity and temperature at the time of collection. Detection limits are 60-120 μg/m^3 for most solvents for a 4 hour sampling period.

A 3M Model 3500 sampler is ideal for obtaining measurements of exposures to multiple solvents in one sitting or in situations where direct observation of sampling may not be possible. This sampler has been compared extensively with results obtained by charcoal tube sampling with excellent correlation between the 2 methods (Table 1). NIOSH will accept sampling methods for industrial hygiene studies that have an overall error rate (defined as bias + 2*(coefficient of variation)) of ±25% or less. As can be seen in Table 1, 3M samplers meet this level of precision for most tested solvents. For in-field sampling, the coefficient of variation with collection by 3M Samplers can be appreciably less than that seen with charcoal tube sampling (Van Den Hoed, et al, 1987).

Further, the 3M Model 3500 sampler has undergone interlaboratory testing against mixtures of n-hexane, and toluene (Periago & Uribe, 1994). Accuracy, reproducibility, and repeatability of the data were determined according to ISO Standard 5725 . n-Hexane levels ranged from 29.6-704 mg/m^3 while toluene levels ranged from 30.7-744 mg/m^3. Repeatability of the n-hexane and toluene data varied from 5.7-20.4% and reproducibility varied from 9.7 to 23.3%.

The 3M Model 3500 sampler has been evaluated for variables that may affect performance (Bertrand & Berthier, 1987). Its saturation point, at 7500 mg/m^3 over 8 hours for most solvents, is well above levels found in the work place. There is no solvent loss after 68 days of storage. Collection efficiency is not affected by orientation between the monitor face and air flow. Airflow will affect collection efficiency at flows <0.01 m/sec (Byeon, et al, 1997). Flows in workplaces (and, by analogy, other ventilated areas) are, however, 30-40 times this level. Further, this monitor can accurately measure solvent levels in highly complex mixtures (Table 1); and it responds rapidly to changes in solvent concentrations and can accurately measure exposure levels over periods as short as 6 minutes (Einfeld, 1983). At very high humidities (90% or greater), measurements for ketones can give erroneously low results (Byeon, et al, 1997). In this study, however, measured relative humidity levels were always <60%)and there were corrections for humidity during the analyses.

Table 1: Precision and Correlation of 3M Samplers with Charcoal Tube Samplers

Chemical validated	Sampling time (hrs)	Exposure level (ppm)	Correlation coefficient with charcoal tube	Overall error (±%)	Reference
MEK	4	275		2	Byeon et al '97

Toluene	4	60		9-14	“
n-Hexane	4	200		12-14	“
n-Hexane	8		0.79		Lauwerys et al ‘83
Tetrachloroethylene	8		0.89		“
n-Hexane		17-91	0.96		Voelte & Weir ‘81
Isopropanol		13.6-76	0.95		“
Trichloroethylene		14.3-89	0.99		“
Toluene		13.9-102	0.99		“
acrylonitrile				17	Rose & Perkins ‘82
trichloroethylene				13	“
Halothane				10	“
Enfluorane				10	“
benzene mixed with gasoline	4	3-60		19	Speilman et al ‘87
benzene	4	3-60		10	“
n-hexane	8		>0.90		Hickey & Bishop
methylcyclopentane	8	0-70	>0.90		“
toluene, 2-methylpentane	8	0-10	>0.90		“:
3-methylpentane	8	0-30	>0.90		“
n-heptane	8	0-75	>0.90		“
n-pentane	8	0-30	>0.90		“
isopentane	8	0-40	>0.90		“
methylcyclopentane	8		Paired T test P<0.05		“
toluene	8	0-20	“		“
trichloroethylene	8		“		“
benzene	8		“		“
MEK	8		“		“
xylene	8		“		“
isopropanol	8		“		“
n-octane	8		<0.90		“
methylene chloride	4	0.9-63		10	Charron et al ‘98
Ethylene glycol monomethyl ether	0.15-8			17	Langhorst ‘84
propylene glycol monomethyl ether				14	“
ethylene glycol				13	“

monomethyl ether					
Benzene	0.25-8	0.7-69		11-14	Prista '81
Gasoline	0.25	507		23	"
n-hexane	0.25			15	"
methyl cyclopentane	0.25	0.7		8	"
toluene	0.25	2		10	"
heptane	0.25	0.4		18	"
toluene	0.25	2.6-5		10-12	"
pentane	0.25	7		12	"
octane	0.25	0.5		15	"
xylene	0.25	5-9		6-20	"
ethyl benzene	0.25	5		6	"
Trichloroethylene	0.25-6			2.3-8.2	Einfeld '83
Styrene	4		0.96		van Den Hoed et al '87
22 Gasoline components		<1-<10	0.99 (overall)		Purdham et al '94
styrene		0.3-40	0.995		Hagberg et al '87
ethyl acetate		8-120	CHECK		"
xylene		3-40	0.98		"
ethyl benzene		1-13	0.98		"

Results

The markers used in this study are solvent-based containing methyl n-butyl ketone (MIBK) and n-butyl acetate (NBA) with the remaining low or non-volatile components including resins, pigments, waxes and oils. Exposure assessment was limited to the highly volatile solvents since brief activities may result in appreciable volatilization. Experiments were conducted in both an unventilated room without air recirculation and a classroom with air recirculation with solvent consumption ranging from 424-1992 mg of MIBK and 192-794 mg of NBA in the unventilated room (Table 2) and 260-898 mg of MIBK and 118-408 mg of NBA in the classroom (Table 4).

Solvent consumption during drawing activities was determined for each individual in each experiment by adding solvent use for all used markers. The results are presented in two ways: average individual consumption for each experiment and total solvent consumption for each experiment, the latter used to model background (area) exposures. In order to determine the contribution of individual activities to exposures, individual solvent consumption was compared with associated individual exposures corrected for background where the latter figure equals individual exposure minus background exposure for the experiment (see Figures 3, 6, and 9).

Unventilated room studies

Trials were run with 1, 3 or 5 users. Table 2 details average individual solvent consumption as well as total solvent consumption in each experiment and Table 3 details average individual exposures and background exposures for each experiment.

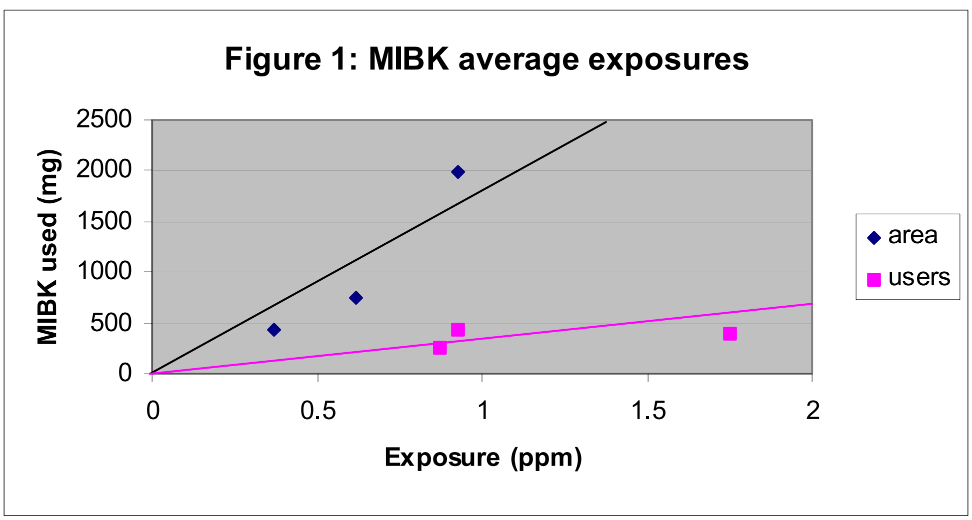
Table 2: Solvent consumed during whiteboard marker use in an unventilated room

# of Users	*MIBK*	*consumption (mg)*	*N-Butyl Acetate*	*consumption (mg)*
	Individual (average)	Overall (sum)	Individual (average)	Overall (sum)
1	424	424	193	193
3	252	755	114	3s43
5	393	1992	179	794

Table 3: Solvent Exposure during Whiteboard use in an Unventilated Room

# of Users	MIBK	exposure (ppm)	N-Butyl Acetate	exposure (ppm)
	Personal	Background	Personal	Background
1	0.93	0.37	0.23	<0.06
3	0.87	0.62	0.21	0.12
5	1.75	0.93	0.27	0.23

Figures 1 and 2 compare average individual (user) exposures to average individual solvent consumption and background (area) exposures to average total solvent consumption for each experiment.



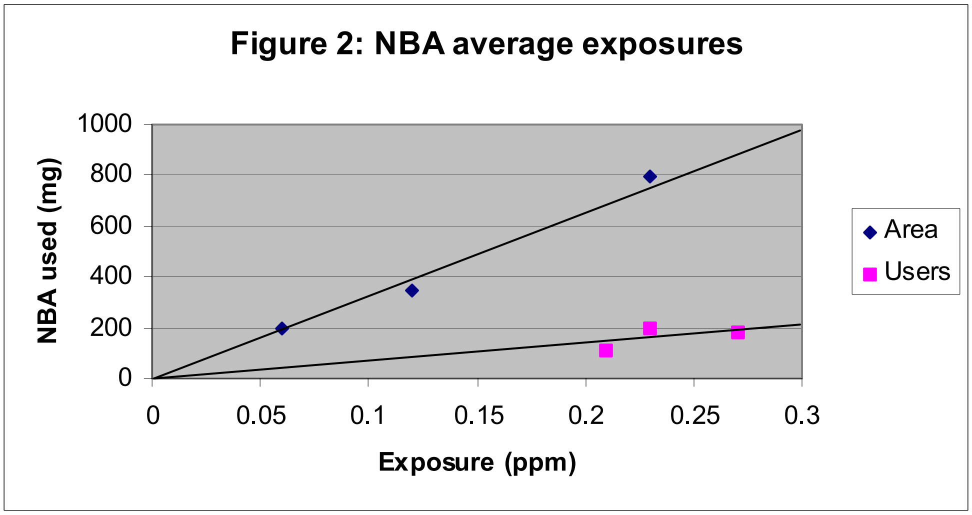
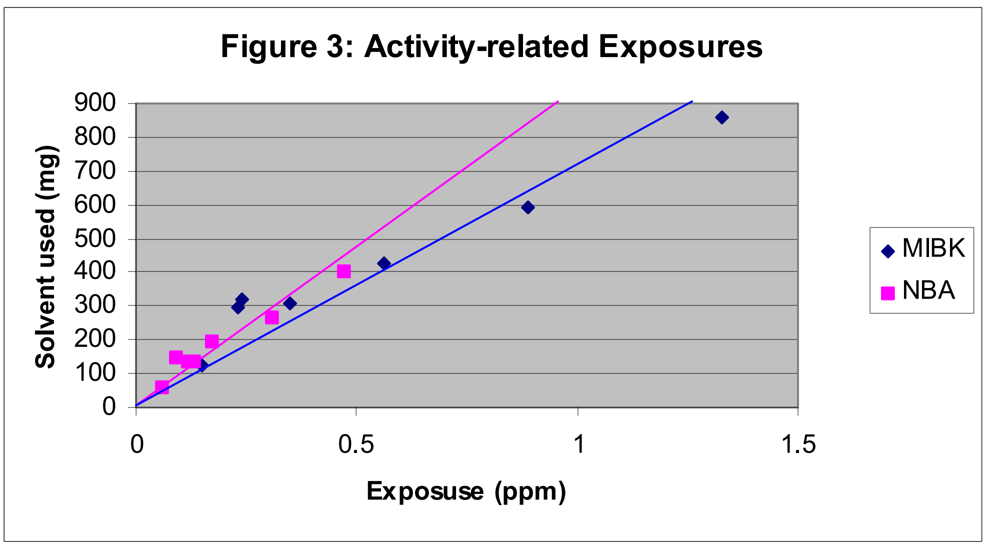


Figure 3 represents the analysis of individual solvent consumption to that component of individual exposure that can be ascribed to individual activities (actual individual exposure-background exposure). A consistent relationship was found for both solvent components of the markers.



School room studies

Trials were run with 1, 2 or 4 users. Table 4 details average individual solvent consumption as well as total solvent consumption in each experiment and Table 5 details average individual exposures and background exposures for each experiment.

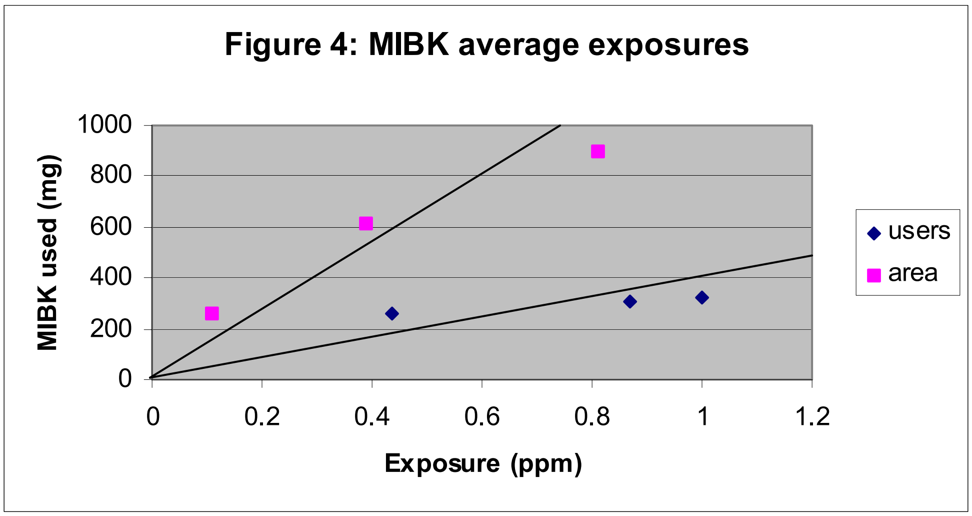
Table 4: Solvent Consumed during Whiteboard use in an Ventilated School Room

# of Users	MIBK	consumption (mg)	N-Butyl Acetate	consumption (mg)
	Individual (average)	Overall (sum)	Individual (average)	Overall (sum)
1	260	260	118	118
2	307	622	139	278
4	323	898	147	408

Table 5: Solvent Exposure during Whiteboard use in a Ventilated School Room

# of Users	MIBK	Exposure (ppm)	N-Butyl Acetate	Exposure (ppm)
	Personal	Background	Personal	Background
1	0.435	0.11	0.14	0.07
2	0.87	0.39	0.21	0.14
4	1.00	0.81	0.34	0.27

Figures 4 and 5 compare average individual (user) exposures to average individual solvent consumption and background (area) exposures to average total solvent consumption for each experiment.



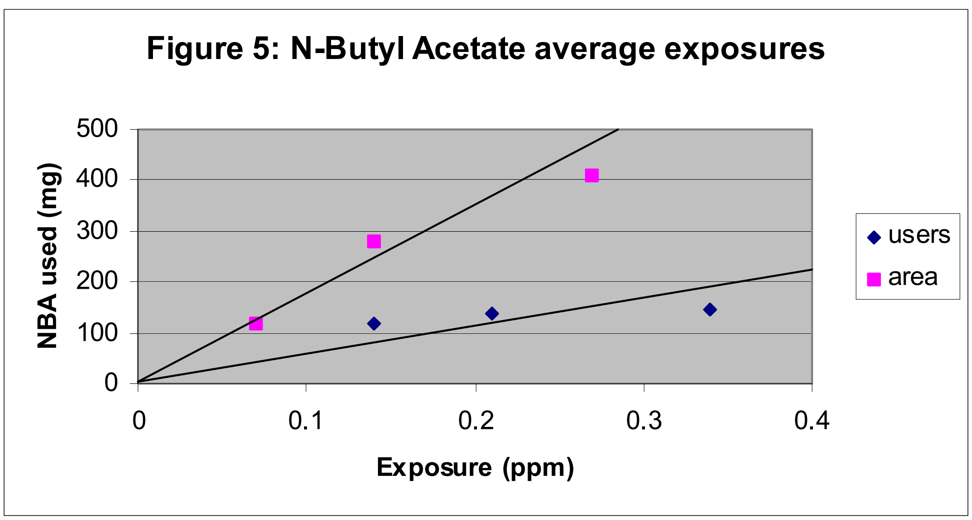
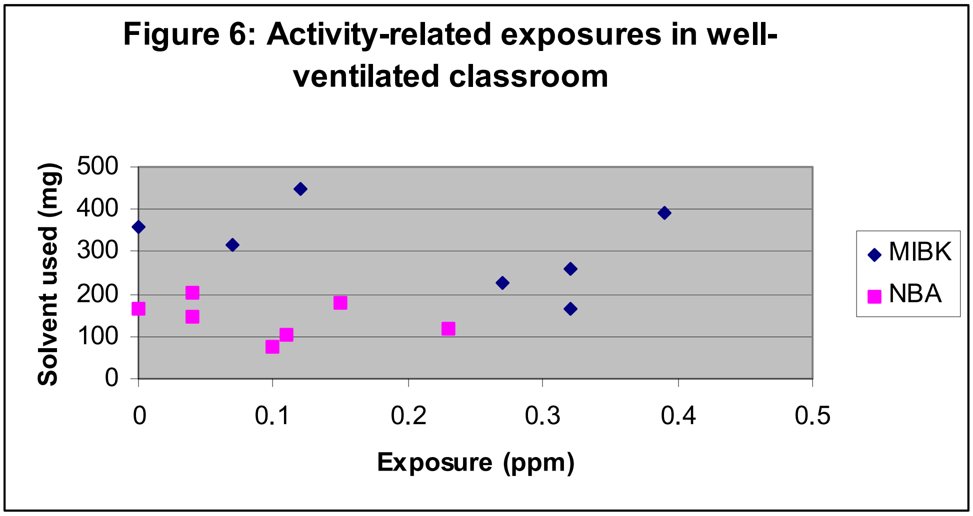
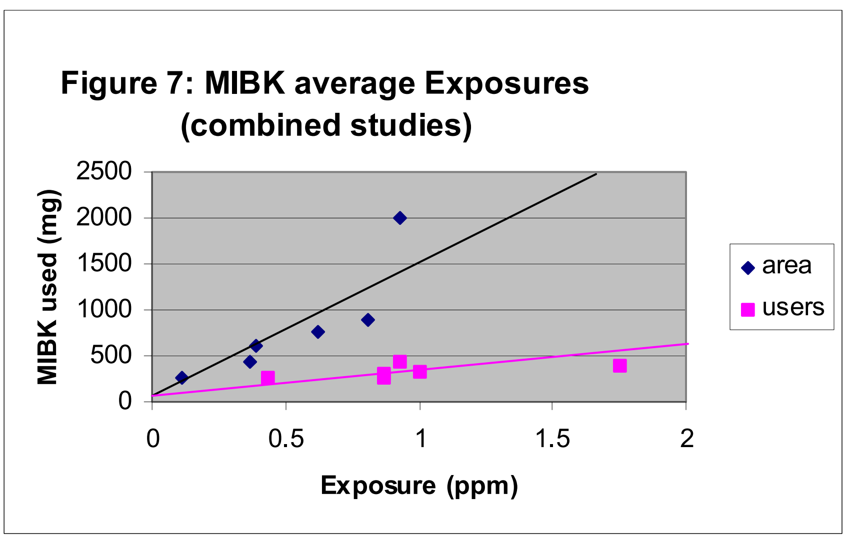


Figure 6 represents the analysis of individual solvent consumption to that component of individual exposure that can be ascribed to individual activities (actual individual exposure-background exposure). No consistent relationship was found for either solvent component of the markers.



Combined studies: relationship between solvent use and exposure

Results for individual users were similar in each study environment, both in magnitude and in the relationship between activity level (as measured by the amount of solvent consumed) and exposure levels. When the results for both arms of the study were combined, a consistent relationship between average solvent consumption and average individual exposures was found (see Figures 7 and 8).



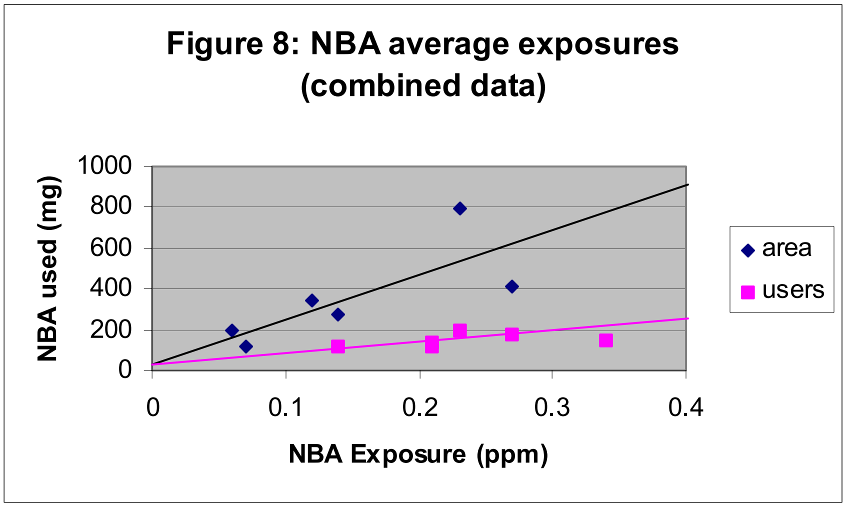
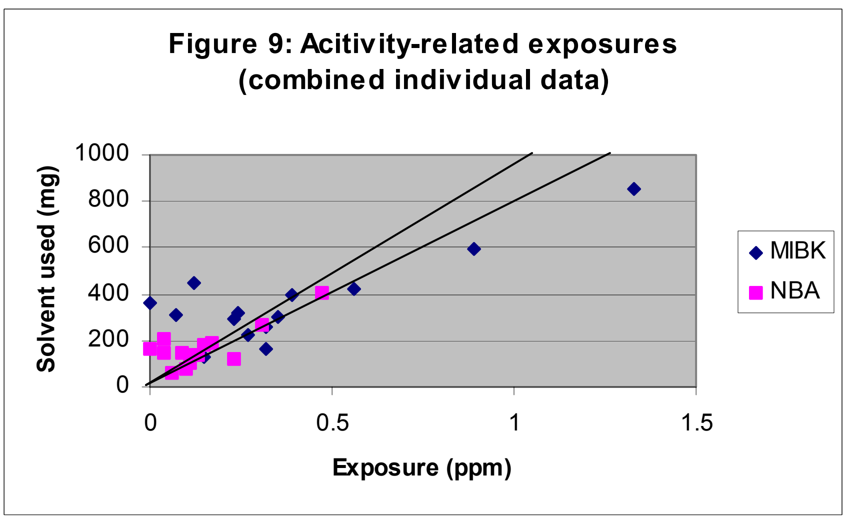


Figure 9 represents the analysis of individual solvent consumption, combining the results for both studies, to that component of individual exposure that can be ascribed to individual activities (actual individual exposure-background exposure). A relationship was found between activity level (solvent consumption) and exposure ascribed to that activity level, though not a strong as for the results for the unventilated room.

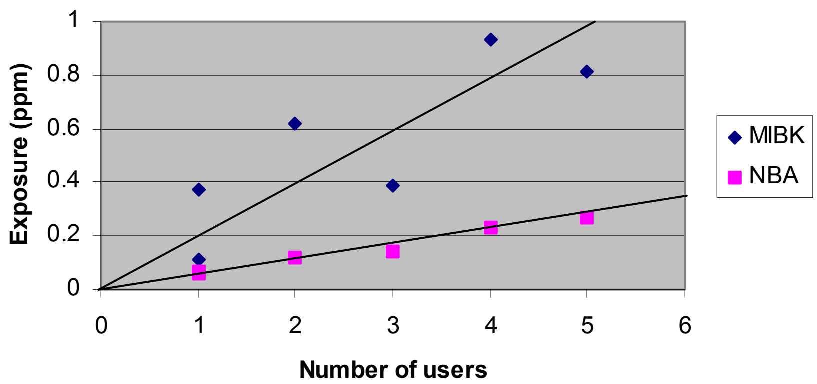


Estimation of exposure when user number increases

Exposure attributable to individual activities was limited, with a maximum activity-related exposure of 1.3 ppm MIBK and 0.47 ppm NBA in the unventilated room and 0.4 ppm MIBK and 0.2 ppm NBA in the well-ventilated school room.

The relationship between number of users and background (area) exposures for the combined study showed an r of 0.79 for MIBK and 0.98 for NBA (figure 10).

Figure 10: User number vs solvent exposure



Assuming that any user will be exposed to the highest average activity related-exposure (personal exposure minus background), then the following relationships describe exposure vs number of marker users in the two situations that were investigated:

Unventilated room
MIBK exposure level (ppm) = 0.56 + 0.19(# of users)
NBA exposure level (ppm) = 0.17 + 0.05(# of users)

Schoolroom
MIBK exposure level (ppm) = 0.19+ 0.19(# of users)
NBA exposure level (ppm) = 0.07 + 0.05(# of users)

For 25 users in an unventilated room, the expected maximum average exposure would be 5.3 ppm for MIBK and 1.4 ppm for NBA, averaged over 4 hours. For 25 users using markers in a similar-sized schoolroom with a recirculating ventilation system, the expected maximum average exposure would be 4.9 ppm for MIBK and 1.3 ppm for NBA

Peak exposures
Although not measured, peak solvent exposures associated with use of these solvent-based markers can be estimated with the general dilutional ventilation equation:

$$C_t = C_i e^{-Qt/V}$$

Where: C_t = concentration (mg/m^3) at time t
P_i = initial concentration
Q = Ventilation rate (m^3/min)
V = room volume (m^3)

Using the area data for 5 users in the unventilated room, the ventilation rate was determined to be 0.4 air changes/hour. Using the area data for 4 users in the schoolroom, the ventilation rate was found to be 0.5 air changes/hour.

Assuming the highest average solvent consumption (424 mg MIBK and 193 mg NBA per user), good circulation (mixing factor of 1) in the schoolroom and somewhat poorer mixing (mixing factor of 0.9) for the unventilated room, then peak exposures and 4 hour average exposures were calculated to be as follows:

Table 6: Peak and average exposure predictions with ventilation modeling

	MIBK (ppm)		**NBA (ppm)**	
	Peak	4 hour average	Peak	4 hour average
Schoolroom	9.8	4.1	3.8	1.6
Unventilated room	10.4	5.3	4.0	2.0

Discussion

Although Hagberg, et al (1987) suggest that activated charcoal may have difficulty collecting highly polar solvents, such as acetates, the results of these studies show a relationship between MIBK and NBA exposures that nearly exactly mirrors their concentrations in the marker inks investigated. These results suggest that activated charcoal is a suitable matrix for measuring exposure to ketones and acetates.

There are two elements that determine exposure: exposure directly related to a user's activity and added background exposure that is determined by the overall level of activity (solvent use) in a room. The former element appears to reflect activity that occurs within 1-2 feet of the user. If the background contribution is subtracted, an excellent relationship is seen between exposure and individual level of activity (r of 0.92 for MIBK and an r of 0.95 for NBA, see Figure 3) in an unventilated room. The largest activity-related exposure (1.3 ppm MIBK and 0.47 ppm NBA) occurred where two users sat 1 foot from each other.

A similar relationship between exposure and the degree of activity is not seen in the well-ventilated schoolroom (Figure 6): air mixing appeared to be sufficient to prevent appreciable breathing zone buildup of solvent vapors associated with individual activities. The highest activity-related exposure (0.39 ppm MIBK and 0.15 NBA) was low compared with activity-related exposures in an unventilated room.

Exposures to solvents from using solvent-based whiteboard markers by multiple users in either a poorly or well-ventilated environment was low. Highest exposures were seen in the poorly ventilated room were the maximum exposure (2.3 ppm MIBK and 0.7 ppm NBA) was seen with 5 users with 2 users working within a foot of each other. There is an excellent relationship between the amount of solvent consumed and background exposure levels (Figures 7 and 8). When translated into number of users vs. background (area) exposure, the relationship remained strong (Figure 10). This relationship allows projection of expected exposures to a number of users. When projected to 25 users, exposures are estimated to average 4.9-5.3 ppm for MIBK and 1.3-1.4 ppm for NBA when measured over 4 hours. When exposures were calculated with the general dilutional ventilation equation, average exposures were similar, ranging from 4.1-5.3 for MIBK and 1.6-.2.0 for NBA. The expected peak exposures from use of these markers by 25 users ranged from 9.8-10.4 ppm for MIBK and 3.8-4.0 ppm for NBA (Table 6) while 4 hour average exposures are projected to range from 4.1-5.3 ppm for MIBK and 1.3-2.0 ppm for NBA. These values compare with ACGIH 15 minute STELs and TLVs for methyl isobutyl ketone of 75 and 50 ppm and of 200 and 150 ppm for n-butyl acetate. It does not appear that heavy use of solvent-based whiteboard markers by students in a classroom situation would likely result in excessive acute solvent exposures.

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