FORMALDEHYDE SCREENING STUDY
WINTER 1993-1994

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INTRODUCTION

The main purpose of the formaldehyde (HCOH) screening study was to determine what the maximum formaldehyde concentrations are in Missoula's ambient air and to determine if these levels pose a threat to human health. The study results will help indicate whether formaldehyde pollution is at levels where mitigation or further studies should be done. Public concern about formaldehyde in Missoula's air has increased because the Clean Air Act amendments mandate that oxyfuels be used in the Missoula Air Stagnation Zone from November 1 through the end of February. While oxyfuels increase formaldehyde emissions from vehicular exhaust, oxyfuels also reduce Carbon monoxide and benzene emissions from vehicles, both of which have adverse effects on human health.

Formaldehyde is listed as a hazardous material by OSHA with an Immediately Dangerous to Life and Health (IDLH) level of 30 ppm and a Time Weighted Average (TWA) limit of 0.3 ppm. The American Society of Heating, Refrigerating, and Air Condition Engineers (ASHRAE) has set a generally accepted limit of 0.1 ppm formaldehyde for indoor air. Formaldehyde is also a suspected carcinogen (American Conference of Governmental Industrial Hygienists, 1993). Formaldehyde is heavier than air and can be detected by its foul odor. Because of its hydrophilic nature, most inhaled formaldehyde is absorbed by the mucus membranes in the upper respiratory tract where it can cause temporary irritation (Jakab, Risby and Hemenway, 1992). Formaldehyde reaches further into the respiratory tract when people smoke, when attached to airborne particles or when concentrations are high. At relatively high concentrations, over 3 ppm, formaldehyde may rarely induce a delayed asthmatic reaction. Formaldehyde also has a transient irritating effect on the mucus membrane around the eye. Once absorbed by the body, formaldehyde is quickly metabolized into non-harmful chemicals.

In Missoula, formaldehyde in the ambient air comes from vehicular exhaust, wood stoves, natural gas, industrial sources such as Louisiana Pacific and White Pine Sash, and it is also formed in the atmosphere by photochemical reactions (NRC, 1981).

Another factor which may cause elevated formaldehyde levels is that Missoula is located in a mountain valley where winter time temperature inversions are common. The resulting poor dispersion could trap formaldehyde, which is heavier than air, in the valley and so cause high formaldehyde concentrations.

MONITORING EQUIPMENT

Passive formaldehyde samplers were purchased from Daniel Grosjean and Associates, Inc. (DGA). The DGA Formaldehyde Passive Sampler consists of a plastic body, called the sampling unit, whose upper stage serves as the diffusion barrier and a lower stage which includes a 2,4-dinitrophenylhydrazine (DNPH) coated filter as the formaldehyde trap. After sampling, the DNPH filter was analyzed at DGA by high pressure liquid chromatography.

The measured sampling rate is 18.8 $\pm$ 1.8 mL per minute and is independent of formaldehyde concentration and sampling duration. The detection limit is 32 ppb per hour, i.e. 4 ppb for an 8 hour sample, 1.3 ppb for a 24 hour sample, ect.. To measure sampler precision, pairs of samplers were co-located in photochemically polluted outdoor air. The average difference between the co-located samplers was 10.2% (Grosjean and Williams, 1992).

SOURCES OF FORMALDEHYDE

The main sources of formaldehyde in Missoula are industry, woodstoves, natural gas and automobiles. The table below gives a brief list of Missoula County formaldehyde sources and the amounts they generate. Industrial emission estimates came from the 1987 Toxic Inventory (Radian, 1988) and other emission estimates were computed based on the 1991 EPA document Locating and Estimating Air Emissions from Sources of Formaldehyde. Formaldehyde produced from slash burning is not included because slash burning does not occur during the winter months when oxyfuels are being used.

TABLE 1
SOURCES OF FORMALDEHYDE

SOURCE	FORMALDEHYDE POUNDS/DAY	FORMALDEHYDE POUNDS/YEAR	% OF TOTAL
Borden Chemical	11.6	4249.9	0.68
Gateway Printing	0.0	1.0	0.00
Louisiana Pacific	297.1	108445.0	17.39
Msla Tissue & Cytology	0.0	0.1	0.00
St. Patrick Hospital	0.3	102.0	0.00
Bonner - Hog Fuel	309.3	112894.5	18.11
- Fugitive	1.5	547.5	0.01
Stone - Hog Fuel	521.1	190201.5	30.51
- Liquor	5.1	1861.5	0.30
Msla White Pine Sash	11.7	4270.5	0.68
TOTAL INDUSTRY	**1157.7**	**422560.5**	**67.78**
Automobile	31.4	11461.0	1.84
Natural Gas	165.8	60517.0	9.71
Woodstove(Fireplace)	353.3	128954.5	20.68
TOTAL	**1708.2**	**623493.0**	

Stone Container and the Bonner mill, which together account for 48.93% of the total formaldehyde emissions, are both located several miles outside of the Missoula city limits. Because of this, the impact on ambient formaldehyde levels in Missoula from these two sources is probably much less than their percent of formaldehyde emissions implies. When the formaldehyde sources of Stone Container and Bonner are ignored, automobiles account for 3.60%, natural gas 19.03% and woodstoves 40.55% of the formaldehyde emissions.

SITE LOCATIONS AND SAMPLING PERIODS

One of the main reasons for the formaldehyde screening study was public concern about the increased formaldehyde production from vehicles using oxyfuels. Consequently, three of the five formaldehyde samplers were placed near intersections while two were placed near the major industrial emitters Louisiana Pacific and Borden Chemical. Two of the samplers were co-located at Malfunction Junction, the intersection of Brooks, Russell Street and South Avenue, which is the busiest intersection in Missoula. Malfunction Junction is also located on the corner of the highest wood stove use grid (1990 CO Emission Inventory, 1990).

The fifth sampler was placed at the intersection of Reserve Street and South Avenue. Even with reduced traffic because of construction on Reserve Street, the Reserve and South Avenue intersection had the highest CO concentrations behind Malfunction Junction during the 1992 Carbon Monoxide Saturation Study. Traffic levels at Reserve and South are now higher, but moving more efficiently, because construction on Reserve Street has been completed. Because of the high traffic and CO levels measured at Reserve and South, a formaldehyde sampler was placed there.

All samplers were run concurrently so that relative levels of formaldehyde could be compared throughout the urban area. In an attempt to monitor the highest formaldehyde concentrations, a total of eight sets of samples were collected during the worst dispersion periods of the winter.

STUDY RESULTS AND PRECISION

Table 2, following, list all of the formaldehyde results from the study. The highest group of readings was from 12/17/93 through 12/31/93, with a high reading of 8.54 parts per billion (ppb) at the MFJ site. The highest single concentration was 8.59 ppb at the South and Reserve sampling site from 1/18/94 through 1/26/94.

Sampler 253 located west of Borden Chemical, at the intersection of Grant and Stockyard, was replaced part way through the study with sampler 220 because 253 was thrown into a field and temporarily lost. Two samples were not collected at the Grant and Stockyard site because of the lost sampler. The final two samples collected at the industrial sites were moved to different locations, dots numbered 2 on the page 5 map, to see if there would be variation in the results. The final two samples did not vary drastically from the earlier samples and no conclusive differences between the industrial sites was noted.

Sampler 250 at MFJ had a time weighted average (TWA) of 2.46 ppb and sampler 251 at MFJ had a TWA of 2.23 ppb. Sampler 252 at South and Reserve had a TWA of 4.03 ppb. Samplers 253 and 220 had a combined TWA of 3.33 ppb and sampler 254 had a TWA of 3.36 ppb. While the industrial sites have higher time weighted averages than the MFJ sites, all three intersection sites have individual readings higher than the industrial sites.

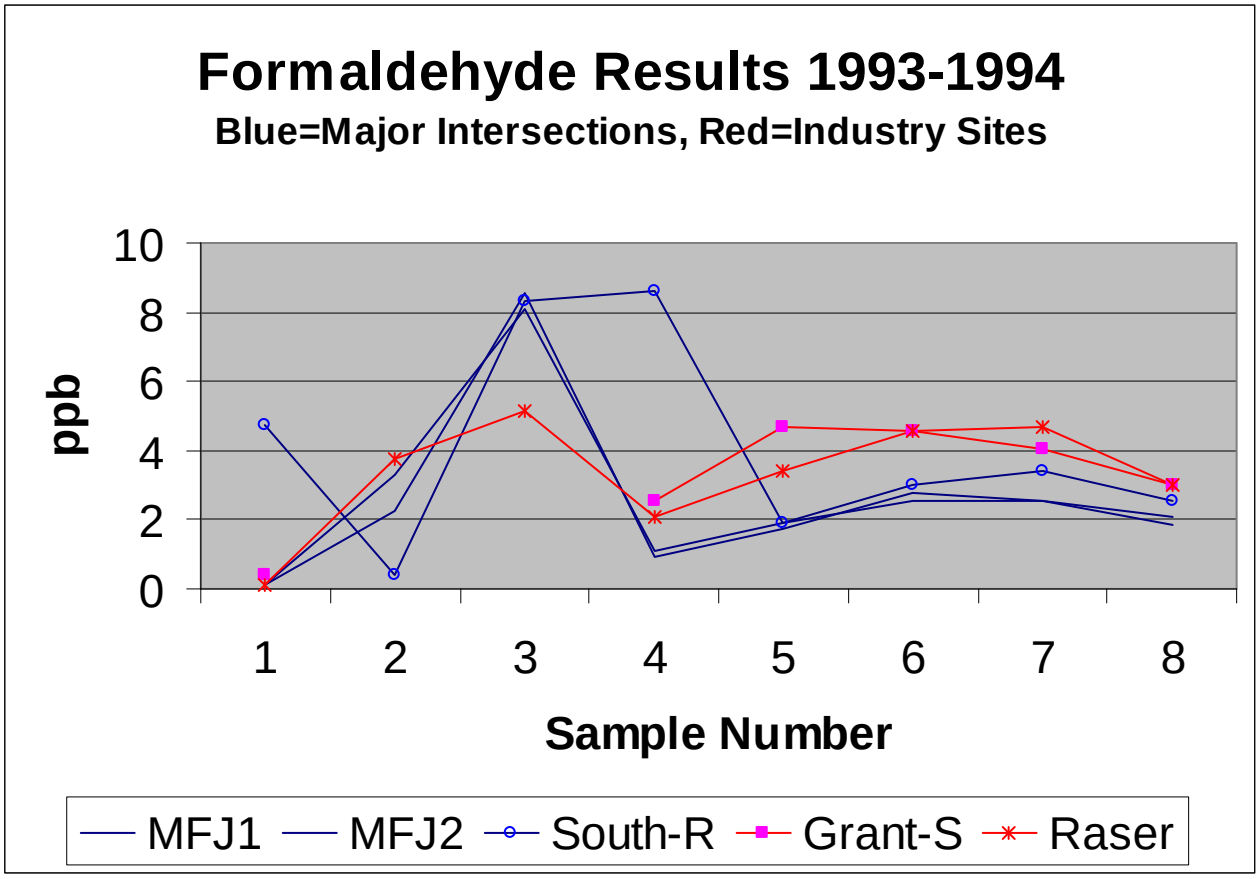
The average daily PM-10 levels, as measured by a Beta Attenuated Mass Monitor located at Boyd Park in Missoula, were 61, 29, 64, 65, 45, 79, 51 and 38 ug/m^3 respectively during the eight sample sets. When ambient PM-10 levels are compared with the formaldehyde results from the five sites, the MFJ samplers #250 and #251 have correlation coefficients of 0.0768 and 0.1809, the South and Reserve site has a correlation coefficient of 0.6183, and the industrial sites #253(220) and #254 have correlation coefficients of -0.0527 and 0.0220 respectively. This suggests that there is minimal correlation between ambient PM-10 levels and ambient formaldehyde concentrations during the winter months when PM-10 levels are below 80 ug/m^3. Under more severe inversion conditions, or higher PM-10 levels, formaldehyde concentrations in the ambient air would most likely be higher than those measured in this study.

The precision of the formaldehyde samplers was assessed by co-locating two samplers at the MFJ site. All eight pairs of samples collected at MFJ were within 1 ppb and 7 of the 8 pairs were within 0.5 ppb. The correlation coefficient between the sets of samples was 0.98630. This indicates that there was a high degree of precision in the sampling technique.

TABLE 2
Missoula Winter 1993-1994 Formaldehyde Study Results

	Location	Start		End		Duration	HCHO	HCHO
Sample #		Date	Time	Date	Time	Days	ug	ppb
1	Malfunction Junction #1	12/14/93	16:30	12/17/93	15:05	2.94	0.09	0.10
2		12/17/03	15:05	12/22/93	16:15	5.05	0.21	3.27
3		12/27/03	14:10	12/31/93	14:52	4.03	0.34	8.12
4		1/18/04	14:20	1/26/94	15:20	8.04	0.07	1.11
5		1/26/94	15:20	2/1/94	14:50	5.98	0.09	1.93
6		2/1/94	15:00	2/6/94	16:20	5.06	0.10	2.53
7		2/25/94	14:55	3/3/94	14:20	5.98	0.12	2.57
8		3/3/94	14:20	3/14/94	16:45	11.12	0.15	1.84
1	Malfunction Junction #2	12/14/93	16:30	12/17/93	16:15	2.99	0.09	0.10
2		12/17/03	16:15	12/22/93	16:15	5.00	0.17	2.28
3		12/27/03	14:10	12/31/93	14:52	4.03	0.35	8.54
4		1/18/04	14:20	1/26/94	15:20	8.04	0.06	0.95
5		1/26/94	15:20	2/1/94	14:50	5.98	0.08	1.71
6		2/1/94	15:00	2/6/94	16:20	5.06	0.11	2.78
7		2/25/94	14:55	3/3/94	14:20	5.98	0.12	2.57
8		3/3/94	14:40	3/14/94	16:40	11.08	0.17	2.08
1	South Ave & Reserve St	12/14/93	16:15	12/17/93	14:55	2.94	0.19	4.74
2		12/17/03	14:55	12/22/93	16:00	5.05	0.10	0.40
3		12/27/03	14:00	12/31/93	14:40	4.03	0.34	8.34
4		1/18/04	14:00	1/26/94	15:00	8.04	0.52	8.59
5		1/26/94	15:00	2/1/94	14:35	5.98	0.09	1.92
6		2/1/94	14:40	2/6/94	16:10	5.06	0.12	3.03
7		2/25/94	14:45	3/3/94	14:10	5.98	0.15	3.43
8		3/3/94	14:10	3/14/94	16:30	11.10	0.21	2.54
1	Grant & Stockyard	12/14/93	16:00	12/17/93	14:30	2.94	0.10	0.39
2		12/17/03	14:30	Vandalism				
3		No Data		Vandalism				
4		1/18/04	13:45	1/26/94	14:45	8.04	0.15	2.55
5		1/26/94	14:45	2/1/94	14:20	5.98	0.21	4.7
6		2/1/94	14:20	2/6/94	16:00	5.07	0.17	4.54
7	N. of Borden	2/25/94	14:15	3/3/94	13:35	5.97	0.18	4.07
8		3/3/94	13:35	3/14/94	16:00	11.10	0.25	3.00
1	Raser Drive	12/14/93	16:00	12/17/93	14:45	2.95	0.09	0.10
2		12/17/03	14:45	12/22/93	15:45	5.04	0.23	3.78
3		12/27/03	13:45	12/31/93	14:30	4.03	0.25	5.15
4		1/18/04	14:00	1/26/94	14:50	8.03	0.13	2.07
5		1/26/94	14:50	2/1/94	14:00	5.97	0.15	3.43
6		2/1/94	14:15	2/6/94	15:50	5.07	0.17	4.55
7	West of L.P.	2/25/94	14:25	3/3/94	13:55	5.98	0.21	4.71
8		3/3/94	13:55	3/14/94	16:10	11.09	0.25	3.00

GRAPH 1
Major Intersection and Industrial Site Comparisons



DISCUSSION AND RECOMMENDATIONS

One of the main objectives of the study was to find out what the highest concentrations of formaldehyde were during the winter and to determine if these levels posed a threat to human health. The highest formaldehyde concentration measured was 8.59 ppb at the South Avenue and Reserve Street site. This is far below the 300 ppb Time Weighted Average exposure limit set by the American Conference of Governmental Industrial Hygienists (ACGIH). But it should be noted that the TWA is an exposure limit for a 40 hour work week, not a limit for continuous exposure that ambient concentrations could give. The Olympia Air Pollution Control Authority of Washington has set an ambient ceiling value of 50 ppb for formaldehyde (EPA, 1988). The most stringent standard for ambient formaldehyde can be found in the state of New York which has set a limit of 4.05 ppb averaged over a one year period. Since the highest TWA during the study was 4.03 ppb at the Reserve and South site and the study was done during poor winter dispersion periods, Missoula'a yearly average is probably significantly below 4.05 ppb. New York arrived at their standard by dividing the 1984-1985 ACGIH TWA exposure limit by an uncertainty factor (EPA, 1988).

When compared to major cities in the world, Missoula has lower ambient air formaldehyde levels. For instance, ambient formaldehyde levels have reached 159 ppb in Sao Paula, Brazil (Kabuto, Tsugane and Hamada, 1990) and a year long study in Los Angeles California had results between 5 and 20 ppb (Grosjean, 1994). These areas are different from Missoula in that over 90% of the formaldehyde in their ambient air is a secondary byproduct of hydrocarbon pollution. The formaldehyde is produced by a photochemical reaction with hydrocarbons emitted by vehicles. Because of Missoula's latitude and climate, photochemically based reactions are unlikely to be a major contributor to formaldehyde levels. In the summer months when photochemical reactions play more of a role in formaldehyde production, Missoula doesn't use oxyfuels and good dispersion prevents elevated hydrocarbon concentrations.

Another area of concern for formaldehyde is indoor air where concentrations are typically between 30-100 ppb in homes and public buildings (Crump and Gardiner, 1989), much higher than Missoula's ambient concentrations of 0.1 ppb to 8.59 ppb. Formaldehyde levels over 100 ppb can cause sensitive individuals to have headaches, nausea, and irritation to the mucus membranes. The primary sources of formaldehyde in indoor air are wood products bonded with urea-formaldehyde resin and insulation. Typically, mobile homes have the highest levels of formaldehyde. The up side to this is that formaldehyde off gassing from building materials has a half life of 30-60 months (Marchant, 1986) so older buildings tend to have lower formaldehyde concentrations.

While the time weighted averages for the five study sites are fairly close, future formaldehyde studies should include sampler sites near industrial areas to catch any exceptional events that may occur. If summer studies are done, industrial sites should be included because the higher temperatures would cause more volatilization of formaldehyde.

Based on this investigation, formaldehyde levels in Missoula's ambient air do not appear to pose a threat to human health. Even so, concentrations should be kept as low as possible because formaldehyde is a suspected carcinogen. Some ways formaldehyde emissions could be lowered include additional pollution control equipment at industrial sources, reduction of vehicular traffic and congestion, and replacement of high formaldehyde emitting stoves. Oxyfuels should continue to

be used because vehicles produce only 1.84% of the formaldehyde. The small increase in formaldehyde produced by vehicles is offset by the more significant decrease in benzene, a known carcinogen, carbon monoxide, and other pollutants.

BIBLIOGRAPHY

1990 Base Year Carbon Monoxide Emission Inventory. Missoula, MT, Missoula City County Health Dept., pp. 23, 1990.

American Conference of Governmental Industrial Hygienists, 1993-1994 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices. 6500 Glenway Ave., Bldg. D-7, Cincinnati, OH 45211-4438, 1993.

ASHARE, Ventilation for Acceptable Indoor Air Quality. Standard 62-1981, 1791 Tullie Circle N.E., Atlanta, Georgia, 1981.

Crump D.R. and Gardiner D., "Sources and concentrations of aldehydes and ketones in indoor environments in the United Kingdom," In: Environmental International. 15, pp. 455-462, 1989.

EPA (Environmental Protection Agency), National Air Toxics Information Clearinghouse. Office of Air Quality Planning and Standards, Research Triangle Park, NC 27711, EPA- 450/5-88-007, July, 1988.

EPA, Locating and Estimating Air Emissions From Sources of Formaldehyde (Revised). Office of Air Quality Planning and Standards, Research Triangle Park, NC 27711, EPA- 450/4-91-012, March, 1991.

Grosjean D. and Williams E., "A passive sampler for airborne formaldehyde," In: Atmospheric Environmental. Vol. 26A, No. 16, pp. 2923-2928, 1992 Pergamon Press Ltd, Great Britain, 1992.

Grosjean D., Daniel Grosjean and Associates, Inc., 4526 Telephone Road, Suite 205, Ventura, CA 93003, interview by author, June 24, 1994.

Jakab G.J., Risby T.H. and Hemenway D.R., "Use of physical chemistry and in vivo exposure to investigate the toxicity of formaldehyde bound to carbonaceous particles in the murine lung," In: Research Report/Health Effects Institute. Oct. (53): 1-39, discussion 41-9, 1992.

Kabuto M., Tsugane S. and Hamada G.S., "Current status of air pollution in Sao Paulo, Brazil: effects and problems associated with the introduction of ethanol-fueled motor vehicles," In: Japanese Journal of Public Health. Tokyo, May; 37(5), pp. 340-346, 1990.

Marchant R., "Exposure to high concentration of formaldehyde, a case study," In: Indoor Air Quality in Cold Climates. D. Walkinshaw, editor, Air Pollution Control Association Specialty Conference, Ottawa, Ontario, April, 1986.

NRC (National Research Council) Formaldehyde and Other Aldehydes. National Academy Press, Washington D.C., 1981.

Radian Corporation, Summary of Toxic Air Pollutant Emission Inventory Survey for Montana. 3200 Progress Center, P.O. 13000, Research Triangle Park, NC 27709, October, 1988.