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September 3, 1974

To: Technical Task Group on Vinyl Chloride Research
Technical Panel on Fluorocarbon Research

Subject: EPA Paper Exposure to Halogenated Hydrocarbons
in the Indoor Environment

Gentlemen:

Distributed herewith are copies of a draft of the
subject paper, which was presented at a recent conference
on public health implications of components of plastics
manufacture.

Sincerely,

Kenneth D. Johnson, Ph.D.
Assistant Technical Director
Air Quality

KDJ/mb

Enclosure

cc: D. P. Duffield, M.D.
Mr. A. W. Barnes
Dr. Tiziano Garlanda
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Exposure to Halogenated Hydrocarbons
in the Indoor Environment

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SECOND DRAFT

For Presentation at

Conference on
Public Health Implications of Components of Plastic Manufacture
Pinehurst, North Carolina
July 31, 1974

INTRODUCTION

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The indoor environment has often been ignored as a significant source of exposure to air pollution despite the fact that levels of pollutants in the indoor air can frequently exceed those concentrations which commonly occur in the outdoor environment. The indoor environment includes that present in a number of circumstances including occupational situations, public buildings, hospitals and the home. The discussion to follow stresses, but is not limited to, consideration of exposures in the home situation. The present paper endeavors to review those instances where indoor air pollutants and particularly halogenated hydrocarbons, may reach concentrations of potential public health significance. In the past there has been considerable attention given to the potential health hazards of chlorinated aromatic compounds such as PCB's and pesticides. To date, however, there has been relatively little attention given to the halogenated aliphatic compounds which are the primary focus of the present paper.

Behavior of Pollutants in the Indoor Environment

Assuming that a given pollutant is chemically stable in the indoor air and that it is present as a result of being generated from an indoor source then its concentration as a function of time may be described by the following equation (1): $C = C_0 e^{(-K \frac{Q}{V} t)}$ (1)

where:

C = concentration at time, t

C₀ = initial concentration at time, 0.

Q = air supply rate in ft³/min

V = room volume, ft³

t = time, minutes

k = a constant to adjust for imperfect mixing

This equation assumes that after time zero the source is turned off and that the air supply into the room is not contaminated by the pollutant in question. If a continuous source for a given pollutant is also present then the problem becomes more complex. Even a small continuous source can greatly affect indoor pollution levels which under certain circumstances may build up considerably (2,3). In the discussion to follow only the simplified situation without a constant source of pollution will be considered, recognizing that this may underestimate exposure in those instances when a constant emission source is present.

In practice, under best mixing conditions, the highest achievable value for k , the mixing constant (shown in equation (1)) is $1/2$. Under these circumstances equation (1) becomes: $C = C_0 e^{(-\frac{Q}{2V}t)}$ (2)

It is apparent from this equation that an important parameter affecting concentration is the turnover rate of air in the room per minute, Q/V . If there is no exchange of fresh air then the equation reduces to a condition in which the concentration at any time is equal to the concentration at time zero. The more frequent is the exchange for fresh air, the more rapid is the concentration of the pollutant decreased.

Let us examine, for example, the decrease in concentration with time predicted by equation (2) under various rates of fresh air exchange. These calculations are shown in Table 1 and in Figure 1. The strong dependence of outdoor concentration upon air exchange rate is illustrated in this Table and Figure. For example, with but one air exchange per hour, at 30 minutes the concentration is nearly 80% of its initial value whereas at 6

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TABLE 1

Dependence of Indoor Concentration Upon Air Exchange
Rates in a Room
Air Exchange Rate

<u>Time</u> (minutes)	<u>Once Per Hour</u> ($Q/v=1/60$)	<u>Twice Per Hour</u> ($Q/v=2/60$)	<u>Six Times Per Hour</u> ($Q/v = 6/60$)
0	Co	Co	Co
15	0.88 Co	0.78 Co	0.47 Co
30	0.78 Co	0.61 Co	0.22 Co
45	0.69 Co	0.47 Co	0.11 Co
60	0.61 Co	0.37 Co	0.05 Co
90	0.47 Co	0.22 Co	0.01 Co
120	0.37 Co	0.14 Co	< 0.01 Co
150	0.29 Co	0.08 Co	-
180	0.22 Co	0.05 Co	-

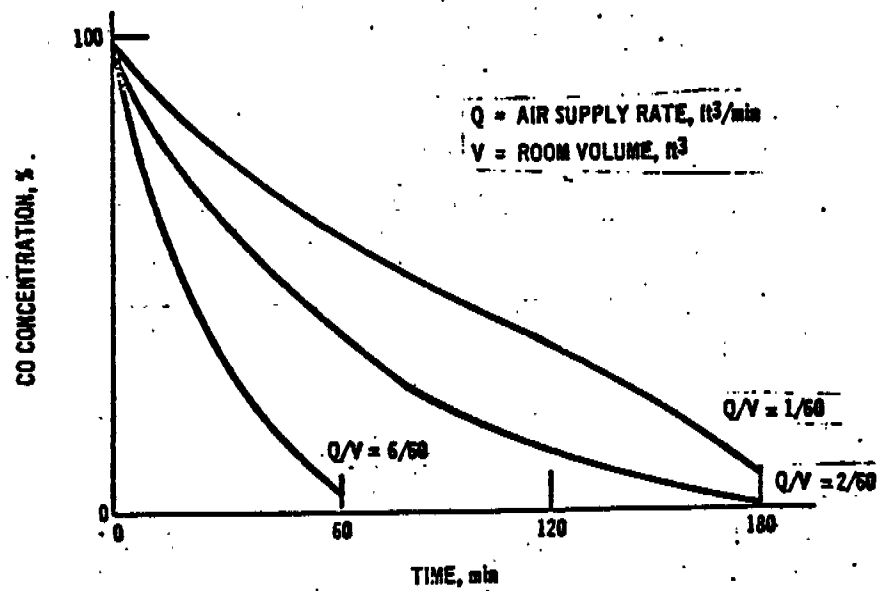


Figure 1. Indoor concentration as a function of air exchange rate and time.

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air exchanges per hour the concentration has dropped to about 20% of the initial value. After 2 hours, at one air exchange per hour the concentration is still better than one-third the initial concentration (C_0), but at 6 air exchanges per hour the concentration has fallen below 1% of its initial value.

Given a functional dependence of concentration with time as shown in equation (2) let us examine some real world measurements of indoor pollution levels (4) to see if they obey this type of relationship. Shown in Table 2 are measurements of propellant concentrations following a 60 second release of a hairspray in a 29,000 liter room. The propellants measured are vinyl chloride and Freon-12. The rate of decay of vinyl chloride parallels that of Freon 12 (shown in Figure 2) suggesting that the vinyl chloride was chemically inert over the time frame examined and under the existing experimental conditions. The effect of air exchange upon concentration in this experiment is similar to that predicted by equation (2) assuming an air exchange rate of 6 times each hour, and considering that the initial high measurements in the breathing zone at time 0 do not reflect complete mixing of the propellants in the room.

Shown in Table 3 are the results of a 30-second aerosol insect spray released in a home laundry room of 21,000 liter volume. The spray was released along the baseboards of the room containing a washer and dryer, sink, clothes and other miscellaneous items. The room has two doors, one leading to a hallway in the house proper and the other leading to the outside. During the experiment, the door to the hall was closed and samples were taken by entering the door to the outside of the house. Sample No. 1, collected one minute after the aerosol was released, showed a concentration of 380 ppm vinyl chloride. Sample No. 4, taken 150

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TABLE 2

Sixty-Second Release of Hairspray in 29,300 Liter Room

Sample	Time	Column I		Column II	
		Vinyl Chloride	Freon-12	Vinyl Chloride	Freon-12
No. 1	Collected at Breathing Zone During Spray	122.7 ppm	62.15ppm	124.4ppm	58.30ppm
No. 2	10 minutes	25.8	11.0	25.1	11.0
No. 3	30 minutes	5.56	2.53	5.2	2.26
No. 4	60 minutes	0.13	0.06	0.12	0.05

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TABLE 3

Thirty-Second Release of Insect Spray in 21,400 Liter Room

Sample	Time	Column I		Column II	
		Vinyl Chloride	Freon-12	Vinyl Chloride	Freon-12
1	Collected one minute after spray	380.1ppm	466.4ppm	383.6ppm	457.6ppm
2	30 minutes later	52.1	54.45	48.7	55.65
3	60 minutes later	24.6	26.40	22.5	25.85
4	150 minutes later	10.3	11.55	9.3	12.10
5	Collected in adjacent hall at 151 minutes	0.83	0.94	0.65	0.83

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minutes after aerosol release, had a concentration of 10.3 ppm vinyl chloride.

A sample taken in the hallway adjacent to the laundry room at 151 minutes contained 0.83 ppm vinyl chloride, indicating spread of vinyl chloride to other areas of the house despite the closed door. Assuming that the initial measurement was not made at a time when there was equal mixing throughout the room, the rate of decay of concentration with time was similar to that which would be expected at an air turnover of twice per hour according to equation (2).

In contrast to the experiment with the hairspray, in which Freon-12 concentrations were about one-half those of the vinyl chloride, Freon-12 levels in the insect spray experiment were 10-20% greater than the vinyl chloride concentrations. Given the frequent sequential use of aerosol products containing Freons such as hairsprays and deoderants, peak exposures to Freon mixtures in excess of 1,000 ppm might result following combined use of such aerosol products in the indoor environment. This raises the possibility that peak exposures to a mixture of Freons following use of aerosol products could exceed the peak exposure recommended for such a mixture in the work environment. The current TLV for Freon-12 is, for example, 1,000 ppm, suggesting that excursions in excess of 1,250 ppm should not be permitted for occupationally exposed individuals(5). Naturally, exposures of the general population should be kept well below those permitted for the occupational population since the general population frequently includes potentially high risk groups not usually found in the work forces.

Shown in Table 4 is a breakdown of propellant use in aerosol products as a function of product category. It is apparent from this table that a

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Table 4. USE OF PROPELLANTS IN AEROSOL PRODUCTS BY PRODUCT CATEGORY

Product Classification	Propellants Used	Frequency Use
Inhalants Containing Bronchodilator drugs (11 products)	Freon 11 (Trichlorofluoro methane) Freon 12 (Dichlorofluoromethane) Freon 114 (Dichlorotetrafluoro ethane)	5/11 11/11 9/11
Mouth Products (6 products)	Freon 12 Freon 114 Freon 1426 (Monochlorodifluoroethane)	5/6 5/6 1/6
Vaporizers (2 products)	Freon 11 Freon 12 Trichloroethane	2/2 2/2 1/2
Hair products (62 products)	Freon 11 Freon 12 Freon 114 Freon 152a (Difluoroethane) Methylene chloride Vinyl chloride Propane Isobutane	53/62 54/62 4/62 5/62 8/62 1/62 3/62 32/62
Women's personal hygiene products (22 products)	Freon 11 Freon 12 Freon 114 Isobutane	5/22 20/22 6/22 2/22
Deoderants and anti- perspirants (38 products)	Freon 11 Freon 12 Freon 114 Freon 142b Propane Isobutane	13/38 37/38 8/38 1/38 1/38 1/38
Foot products (9 products)	Freon 11 Freon 12 Freon 114	8/9 9/9 1/9
Miscellaneous products for personal use (18 products)	Freon 11 Freon 12 Freon 114 Isobutane Propane	7/18 15/18 3/18 2/18 2/18

number of halogenated hydrocarbons are employed as aerosol propellants. Depending upon the frequency and patterns of use of aerosol products among the population, a substantial number of individuals may be repeatedly exposed to these compounds. By far the most commonly used propellants as illustrated in Table 5 are Freon-11 and Freon-12.

Recently published studies of instantaneous Freon-11 and Freon-12 concentrations in the indoor environment taken at random confirm the presence of measurable quantities of these pollutants in the indoor air (6). Levels of Freon-12 in homes, for example, exceeded 500 ppb and were generally much greater than simultaneous outdoor concentrations which usually measured 1 ppb or less. In one study a measurement of Freon 12 in a beauty shop indicated a concentration of 370 ppb (6). A study of Freon-12 levels in a beauty shop conducted by the Environmental Protection Agency found a concentration of 3,000 ppb or 3 ppm averaged over a 15 minute period. In this experiment no vinyl chloride was identified.

Apart from aerosol propellants, another important source of exposure to halogenated hydrocarbons in the indoor environment may be from the active ingredients contained in aerosol products. For example, aerosol spot removers used for clothing, carpets, upholstery and wallpaper may frequently contain perchloroethylene as the active ingredient. Though the concentration of perchloroethylene in such products often is not identified on the label, it is conceivable that the proportion of active ingredients could be similar to the quantity of propellant in these products. Under these circumstances, peak concentrations of perchloroethylene well in excess of 100 ppm might occur during and immediately following spraying as judged from the data in

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Table 5. OVERALL USE OF PROPELLANTS IN 168 AEROSOL PRODUCTS		
Propellant	Frequency of Use	Percent
Freon 11	93/168	55.4
Freon 12	153/168	91.1
Freon 114	36/168	21.4
Freon 142b	2/168	1.2
Freon 152 a	5/168	3.0
Isobutane	37/168	22.0
Methylene chloride	8/168	4.8
Propane	6/168	3.6
Trichloroethane	1/168	0.6
Vinyl chloride	1/168	0.6

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Tables 2 and 3. It is noteworthy that the TLV for perchloroethylene is 100 ppm with excursions recommended not to exceed 150 ppm (5). Accordingly, aerosol products containing perchloroethylene may, under certain circumstances, result in exposures among the general population which exceed established exposure limits for industry.

Another important source of indoor exposure to halogenated hydrocarbons may be from solvents. Such products contain volatile components which could build up to high concentrations in the indoor air. Consider a substance such as trichloroethylene, a structural analogue to vinyl chloride, which is used for a variety of purposes, in dry cleaning, as a degreasing agent, and as an anesthetic. At 12°C (54°F) TCE has a vapor pressure of 40 mm Hg and at 20°C (68°F) TCE has a vapor pressure of 60 mm Hg. In contrast, water at 12°C has a vapor pressure of 11 mm Hg and at 20°C a vapor pressure of 18 mm Hg. Consequently the tendency for trichloroethylene to vaporize is greater than that of water, which does not attain a vapor pressure of 60 mm Hg until 42°C (108°F). Should the atmosphere above trichloroethylene reach only 0.1% of saturation then at 20°C the concentration of trichloroethylene would be nearly 80 ppm. The threshold limit value for TCE is currently set at 100 ppm(5). Naturally with good ventilation TCE would never reach 80 ppm but under certain situations, air exchange may be low and TCE used in a closed space could build up to appreciable airborne concentrations.

Shown in Table 6 are the predicted indoor levels for some commonly used solvents assuming that these attain a concentration only 0.1% of their saturation level in the air. In this regard it is noteworthy that carbon

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Table 6. PREDICTED INDOOR CONCENTRATIONS OF HALOGENATED HYDROCARBON SOLVENTS
ASSUMING THAT THEY REACH 0.1% OF SATURATION LEVELS

Solvent	Temperature (°C)	Predicted Indoor Air Concentration (ppm)
Trichloroethylene	20	80
Tetrachloroethylene	26	26
Trichloroethane (1,1,2)	21	26
Trichloroethane (1,1,1)	20	130
Carbon tetrachloride	23	130
Methylene chloride	24	520

tetrachloride, trichloroethylene and tetrachloroethylene (perchloroethylene) have been detected in either the ambient or the indoor air (6,7).

For example, one study in Los Angeles County in 1966 estimated that emissions of hydrocarbons into the atmosphere from organic solvent usage comprised better than 20% of all hydrocarbon emissions, (8) the majority of emissions coming from gasoline-powered motor vehicles. Of the estimated 590 tons emitted per day from organic solvents, 88 tons per day were attributed to halogenated hydrocarbons, including trichloroethylene and tetrachloroethylene. Given the similarity of chemical structure between trichloroethylene and vinyl chloride one would desire to study the health implications of this substance in much greater depth. (3)

In a study of the airborne environment near a solvent recovery plant in Maryland (7) levels of carbon tetrachloride in the ambient air were commonly measured in the ppm range. The levels of carbon tetrachloride indoors were sometimes 3-4 times greater than those which were measured outdoors. At times concentrations of CCl₄ of 10-45 ppm were measured inside a house when levels outside were 1 ppm. The highest indoor concentration of carbon tetrachloride recorded was 90 ppm. These large differences in indoor/outdoor concentration may reflect buildup of indoor concentrations from an outdoor source measured at a point in time immediately following dramatic reductions in outdoor concentrations. The possibility, of course, must also be considered that an indoor source of carbon tetrachloride also existed.

A potentially important source of indoor exposure to halogenated hydrocarbons may be from use of such compounds as anesthetic agents. It

has already been noted that trichloroethylene continues to be used as an anesthetic, particularly in oral surgery. Vinyl chloride, a structural analogue to trichloroethylene and a recently identified carcinogen and liver toxin has similar neurologic action, and once was considered for use as an anesthetic. Ethylene, though not containing chlorine, has also been used as an anesthetic. Under these circumstances one wonders whether potential for carcinogenic activity and/or liver toxicity exists for unsaturated halogenated compounds with anesthetic activity such as trichloroethylene. If so, a possible health risk may exist not only for patients but also for personnel who day in-day out administer these compounds. A number of other halogenated compounds besides trichloroethylene are also frequently used as anesthetics. These compounds include halothane and methoxyflurane. Though not unsaturated, these latter compounds may require reexamination in terms of their potential for toxic activity, particularly to the liver. Methoxyflurane combines an ether structure with that of a halogenated aliphatic compound and its structural similarity to the chloromethyl ethers should not be overlooked. Chlorform, also halogenated, is yet another anesthetic which is extremely toxic to the liver. It is noteworthy that divinyl ether, while not a halogenated compound, in some respects is analagous in structure to trichloroethylene and vinyl chloride and also represents an anesthetic with established liver toxicity.

It is evident from this brief discussion that a number of halogenated hydrocarbons have been documented and/or are suspected to be present in the airborne environment both indoors and out. What data as are available suggest that indoor levels of these substances are frequently much greater

than are found outdoors, though the source of indoor home contamination may frequently originate from emissions into the ambient air.

Health Implications

In assessing the risk to health for the general population from exposure to a given air pollutant one must consider the inherent toxicity of the material in question, the range of concentrations which may be present in the air, and the probability that members of the population may be exposed to these concentrations. If one were to examine the halogenated hydrocarbons on the basis of the above criteria, many compounds in this class would have to be considered as potential health risks for the general population.

In viewing this class of materials it is instructive to compare the peak indoor concentrations for several halogenated hydrocarbons with those of other air pollutants for which ambient air quality standards have already been set. In making this comparison it is recognized that the relative concentrations are by no means indicative of relative toxicity and that differences are being accentuated by comparing peaks with concentrations over longer averaging periods. On the other hand these comparisons are suggestive of the relative increased indoor atmospheric loading with halogenated hydrocarbons that can occur and of the existence of a potentially important class of air pollutants whose health implications have heretofore not been adequately examined. These contrasts are illustrated in Table 7. In assessing these data one must also recognize that halogenated hydrocarbons present in the ambient air may add to the exposure attributable to indoor

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TABLE 8

Comparative Atmospheric Loading Between
1 ppm Vinyl Chloride and Benzo(a)pyrene

<u>Comparisons</u>	<u>Weight per Volume Comparison</u>	<u>Molecules per Volume Comparison</u>
VC(1ppm)/BaP (10 ng/m ³ , annual average in ambient air)	260,000/l	1,000,000/l
VC(1ppm)/BaP (28-144 ng/m ³ , reported indoor concentrations)	(18,000-93,000)/l	(72,000-372,000)/l

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hydrocarbons should also be examined for their potential effects upon CO metabolism? Home cleaning agents in aerosol form have the potential to exceed accepted occupational exposure limits for perchloroethylene. Are there additional aerosol products which unknowingly may also have the potential to exceed exposure limitations established for occupational situations? Clearly the multitude of aerosol products commercially available represent an important source of exposure to halogenated hydrocarbons, as do solvents and anesthetics. Exposure to these substances is greatly accentuated in the indoor environment where there is less opportunity for dispersion. Since the activity patterns of the general population includes a substantial portion of time spent indoors, the cleanliness of the indoor air becomes an important consideration.

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Table 7. COMPARISON OF PEAK INDOOR AIR MEASUREMENTS FOR HALOGENATED
HYDROCARBONS WITH PRESENT AMBIENT AIR QUALITY STANDARDS

Substance	Peak Indoor Concentration (ppm)	Ambient Air Quality Standard (ppm)
Vinyl Chloride	380	
Freon 12	466	
Carbon Tetrachloride	90	
SO ₂		0.14 ppm (24-hr. average)
NO ₂		0.05 ppm (annual average)
CO		35.00 ppm (1 hour average) 9.00 ppm (8 hour average)
Ozone		0.08 ppm (1 hour average)

concentrations and that halogenated hydrocarbons present outdoors may also participate in photochemical reactants yielding other undesirable products.

Shown in Table 8 are comparisons of relative atmospheric loading on a weight per volume basis and on a molecule per volume basis between vinyl chloride at 1 ppm and benzo(a)pyrene as typically found in the ambient air (10 ng/m^3) and as reported to occur in the indoor air ($28\text{--}144 \text{ ng/m}^3$).

This comparison does not directly reflect relative toxicity between vinyl chloride at 1 ppm and BaP in the air. On the other hand, the relative increased atmospheric loading of 1 ppm vinyl chloride compared to benzo(a)-pyrene, a suspected airborne carcinogen is worthy of note.

Observations such as those discussed in this paper strongly suggest that the general population is currently exposed to substantial quantities of halogenated hydrocarbons in the indoor environment. The health implications of many of these compounds are not well understood. For example, the preponderance of studies on Freons, commonly used as aerosol propellants, involve consideration of acute, but not chronic effects. Accordingly the carcinogenic potential for these compounds cannot readily be dismissed. Though Freons are considered to be chemically inert in the environment this assumption cannot be extended to biological systems. Available data suggest that short term exposures to Freons in man may result in cardiac arrhythmias. The possible effect of such exposures upon individuals already prone to arrhythmias such as those with atherosclerotic heart disease must thus be considered. Use of aerosol products containing methylene chloride combined with Freons may further stress the cardiovascular system by increased endogenous formation of carbon monoxide. How many other halogenated