VINYL CHLORIDE;
The Control of Residual Vinyl Chloride Monomer in PVC Water Pipe

A technical report prepared by the
UNI-BELL PVC PIPE ASSOCIATION

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ABSTRACT

Vinyl Chloride Monomer (VCM) is the basic building block in the manufacture of polyvinyl chloride – commonly called PVC or vinyl. The end product, polyvinyl chloride, produced from VCM in a complex organic chemical reaction, is not a carcinogen. On the contrary, it is used extensively in the medical and health-care industries in many highly sensitive applications, e.g., blood bags, plasma tubing, dialysis units, etc.

Polyvinyl chloride cannot breakdown or degrade in service into VCM. Since the inception of research and investigation of the carcinogenic properties of VCM, the PVC industry has executed a comprehensive and extensive program that has reduced VCM residuals to the extremely low levels which can be considered clearly safe.

As an additional safeguard, beyond those provided in the controlled manufacture of PVC resin, the PVC pipe industry implemented in 1976 an extensive self-regulation program executed by the National Sanitation Foundation (NSF). Through independent third-party inspection, testing, and listing, it is required that residual VCM in PVC potable water pipe be limited to a level which insures no detectable migration of VCM into potable water using analysis technology sensitive to the extremely low level of two parts per billion. (Two parts per billion can be described as two seconds of time in 31.7 years.)

A huge factor of safety has been self-imposed by the PVC pipe industry limiting human exposure to VCM in drinking water. With an understanding of the effort expended and cost incurred by the industry to insure that PVC pipe cannot create a health hazard, and with an understanding of the safeguards provided by NSF Standard 14, the concerned citizen can accept without fear the use of PVC potable water pipe.

CTL015526

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TABLE OF CONTENTS

CTL015554

CTL015529

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VINYL CHLORIDE; The Control of Residual Vinyl Chloride Monomer in PVC Water Pipe

INTRODUCTION

Carginogens, or substances which can induce cancer, deserve serious concern. On January 22, 1974, a major manufacturer of polyvinyl chloride (PVC) resin, the basic raw material for many PVC products including pipe, reported that three plant workers had died from hemangiosarcoma of the liver, a rare form of liver cancer. Over a period of time, careful investigation revealed that these and other workers (less than 40) who had been exposed to high concentrations of vinyl chloride gas over a period of years while working in polymerization plants had contracted the disease. The fact that the incidence of the disease in a hugh worker population (over one million workers worldwide employed over a period of years) was extremely low offers little comfort.

Even though the tragic effects of exposure to vinyl chloride monomer (VCM) were generally limited to polymerization workers, PVC pipe manufacturers immediately became seriously involved in this matter. Although a PVC pipe manufacturer does not produce or process VCM in his pipe plant, he must be concerned about residual vinyl chloride monomer (RVCM) which may remain unreacted in PVC resin received at the pipe plant.

RVCM in PVC resin can diffuse or migrate out of the resin. The pipe manufacturer must exercise proper controls to limit exposure to VCM. He must:

1. Limit pipe-plant worker occupational exposure to VCM which could migrate into the air. This is mandated in U. S. Occupational Safety and Health Administration (OSHA) regulations.[11]
2. Eliminate the potential for significant migration of RVCM from PVC water pipe into potable water.

This technical report will review and summarize the changes in technology and the stringent controls imposed to insure that PVC pipe cannot be a source of a health hazard, to insure that the concerned citizen can accept without fear the use of PVC potable water pipe.

VINYL CHLORIDE MONOMER

Vinyl chloride monomer (VCM) is the basic building block in the manufacture of polyvinyl chloride – commonly called PVC or vinyl.[25] VCM is produced by chemically reacting ethylene and chlorine to create a monomer, a small carbon-based molecule. (See

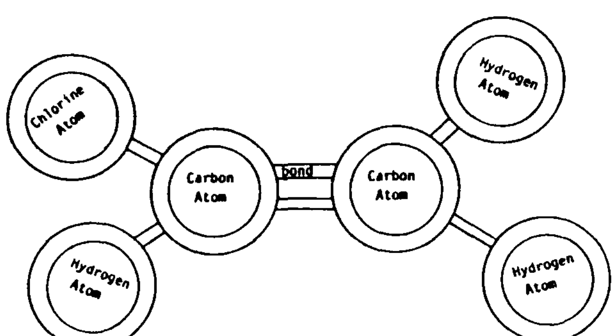
Figure 1) This monomer is a volatile gas which can be polymerized to produce PVC. Polymerization is a reaction which bonds the vinyl chloride monomers into a much larger molecule or polymer known as polyvinyl chloride (PVC).[25]

Polyvinyl Chloride is not Carcinogenic. The end product, PVC, produced through the polymerization of VCM is not a carcinogen. On the contrary, it is used extensively in the medical and health-care industries in many highly sensitive applications, e.g., blood bags, plasma tubing, food wrap, etc. PVC is, of course, used to manufacture millions of miles of potable water pipe every year.

Chemists understand that common table salt is derived through the chemical reaction of two extremely toxic substances – sodium and chlorine. Only through use of a great concentration of energy in a complex chemical reaction can table salt be reduced to its toxic components. The average citizen is comfortable in his knowledge that the reaction cannot occur in common use. In the same sense, PVC cannot break down or degrade in service into VCM. Therefore, PVC poses no threat as a carcinogen.

Residual Vinyl Chloride Monomer. Why then must PVC pipe manufacturers be concerned about VCM? In the process of polymerizing VCM in the manufacture of PVC resin, trace amounts of unreacted monomer may remain entrapped within the PVC resin particles.[3] This residual vinyl chloride monomer (RVCM) immediately begins diffusion or migration from the PVC.[4, 5, 22] If excessive RVCM exists in PVC resin received at a pipe plant, migration of the monomer into the plant working atmosphere could represent an occupational hazard for workers.[11] If PVC pipe were manufactured with high levels of RVCM, migration of the monomer in significant levels into water conveyed by the pipe could be projected.

FIGURE 1. VINYL CHLORIDE MONOMER (VCM)



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CTL015552

CONCLUSION

Since January 1974, when vinyl chloride was identified as a hazardous material, the PVC industry, working closely with the U. S. Government, has successfully implemented sweeping changes in manufacturing technology. Today, the hazards of occupational exposure to vinyl chloride in PVC manufacturing and processing plants have been successfully controlled and limited to the extremely low levels considered safe by OSHA.

Extensive research has been conducted in the laboratory and in the field to determine if the consuming public has been exposed to unsafe levels of vinyl chloride contaminant in potable water conveyed through PVC water pipe. Although laboratory research, theoretical model projections, and thorough field evaluation have demonstrated little cause for concern, the PVC pipe industry prevailed on National Sanitation Foundation in 1976 to implement a tough RVCM monitoring and control program for PVC water pipe production. The NSF certification program remains in force today and has resulted in an impressive improvement in industry control of RVCM in PVC water pipe.

Although a huge factor of safety has been self-imposed by the PVC pipe industry to limit human exposure to VCM in drinking water, such extreme precautions are justified when safeguarding human health. With an understanding of the effort expended and cost incurred by the industry to insure that PVC pipe cannot create a health hazard, the concerned citizen can accept the use of PVC water pipe without fear.

EVOLUTION IN PVC RESIN MANUFACTURING TECHNOLOGY

The initial response to the discovery that VCM could be a carcinogen captured great attention from the manufacturers of PVC products, the plant workers and the media. Prior to the discovery of its apparent carcinogenicity, VCM had been used in many human exposure applications such as propellant in aerosol cans and surgical anesthesia with no recorded or known problems. The effort prior to that time to limit RVCM in PVC during the manufacturing process was influenced by economic pressures. Obviously, the PVC resin manufactuerers were motivated to reclaim RVCM as an effort to improve efficiency in the use of raw materials. Their efforts were limited to that extent deemed economically justifiable. The discovery of apparent VCM carcinogenicity forced immediate changes in technology to safeguard human health.[12, 14]

OSHA Regulations on Occupational Exposure. A major effort was launched by the United States Occupational Safety and Health Administration (OSHA) to investigate and determine the nature and extent of the occupational hazard created by VCM in the manufacturing facilities which process either the monomer or PVC containing residual monomer. OSHA developed stringent regulations for control of occupational exposure to VCM in October 1974.[11] The agency set a maximum permissible exposure limit for VCM at 1 ppm (part per million) averaged over any 8 hour period and a ceiling of 5 ppm averaged over any period not exceeding 15 minutes.[11] OSHA exempted manufacturers from the requirement to implement a number of tough monitoring and control procedures if the levels of airborne VCM were continually held below an "action level" of 0.5 ppm. Immediately, processors of PVC resin, such as pipe manufacturers, wished to comply with the "action level" and demanded PVC resin from their suppliers which contained low levels of RVCM thereby facilitating efforts to limit occupational exposure to VCM to the 0.5 ppm level assumed safe by OSHA.

It should be noted that OSHA's "action level" can be considered safe with a huge factor of safety. Countless PVC resin plant workers through the years worldwide, had been exposed to very high concentrations of VCM in their work environments, concentrations which far exceeded 1000 ppm for extended periods of time. In spite of such serious exposure to a large worker population, the tragic effects of VCM carcinogenicity were apparently limited to less than 40 cases. However, hazard to human health can justify extreme measures. The victims gained little solace from knowledge that their numbers were so few.

Impact of OSHA VCM Regulations. The impact of OSHA's occupational exposure regulations of the PVC pipe industry has been great as demonstrated by the following data. In June 1974 new PVC resin samples were gathered by Johns-Manville Corporation on a random basis from ten PVC pipe plants. In the ten resin samples, the average RVCM was 822 ppm.[21] (See Table 1) PVC resin samples were again gathered and analyzed in December 1974. As shown in Table 1, the average RVCM concentration had fallen to 349 ppm.[21]

TABLE 1

RVCM CONCENTRATION IN PVC RESIN[22]

PVC RESIN SUPPLIER	RVCM RESULTS* JUNE 1974	RVCM RESULTS* DECEMBER 1974
A	259	331
	1224	873
B	779	135
	197	23.2
C	189	44
D	576	1830
	2060	
E	670	23.5
F	1330	18.6
	935	
G		40.4
	AVG RVCM = 822	AVG RVCM = 349

*REPORTED IN PPM ON A WT/WT BASIS

In June-August, 1975 investigation revealed that RVCM levels in PVC resin supplied to PVC pipe manufacturers had been further reduced. (See Table 2). Eighty-four (84) PVC resin samples taken from materials supplied by nine PVC resin manufacturers were analyzed for RVCM.[21] The average RVCM concentration had fallen to 30.2 ppm.[21] Note that only two of the nine manufacturers were lagging behind in improving their RVCM control technology. If those two manufacturers' samples had not been included in the investigation, the average RVCM concentration had fallen to 10.5 ppm in PVC pipe resin.[21]

By 1977, most PVC pipe manufacturers had established purchasing specifications for PVC pipe resin which required RVCM levels certified at or below 10 ppm. To meet these requirements the resin manufacturers dedicated substantial investment and efforts to the development and implementation of sophisticated RVCM "stripping" technology in their operations. Today, PVC pipe manufacturers have little difficulty limiting occupational VCM exposure to levels far lower than the 0.5 ppm "action level" established by OSHA. The

CTL015533

proper RVCM control programs in production of PVC water pipe experienced some problems passing NSF inspection and testing. Table 11 demonstrates the progress achieved in the NSF RVCM monitoring program incorporated into the Standard 14 PVC pipe certification program.

The full impact of the NSF certification program on control of RVCM in PVC water pipe became apparent as early as 1978. Table 12 demonstrates the improvement in RVCM control achieved by PVC pipe manufacturers over the span of one year. It is reasonable to make the following assumptions based on Tables 11 and 12:

- At least 98% of the PVC pipe manufactured today in North America contains less than 10 ppm RVCM.
- Most of the PVC pipe manufactured today in North America contains less than 1 ppm RVCM.

TABLE 11

NSF RVCM MONITORING RESULTS[17]

YEAR	NO. SAMPLES TESTED	PASS[1] (%)	NON-DETECTABLE (ND)[2] (%)
1977	412	93.7	38.1
1978	423	97.4	52.7
1979	664	97.0	46.1
1980[3]	248	98.4	41.1

[1] Based on MCL $\leq$ 10 ppm in PVC pipe or fittings (reference: NSF Standard 14); all failed samples are retested and enforcement procedures followed if required. Retest data are not included in these figures.

[2] For routine analyses, RVCM $<$0.5 ppm is reported as ND.

[3] Samples through June 30, 1980.

TABLE 12

IMPROVEMENT IN RVCM CONTROL
NSF ANALYSIS OF RVCM LEVEL IN PVC WATER PIPE[16]

RVCM MONITORING TIME PERIOD	NUMBER OF SAMPLES	5 PPM<RVCM≤10 PPM NO.	%	50 PPB<RVCM≤5 PPM NO.	%	RVCM≤50 PPB NO.	%
Feb. thru Nov 1977	332	19	5.7	185	55.7	106	31.9
Dec thru Jan 1978	80	5	6.3	20	25.0	51	63.8

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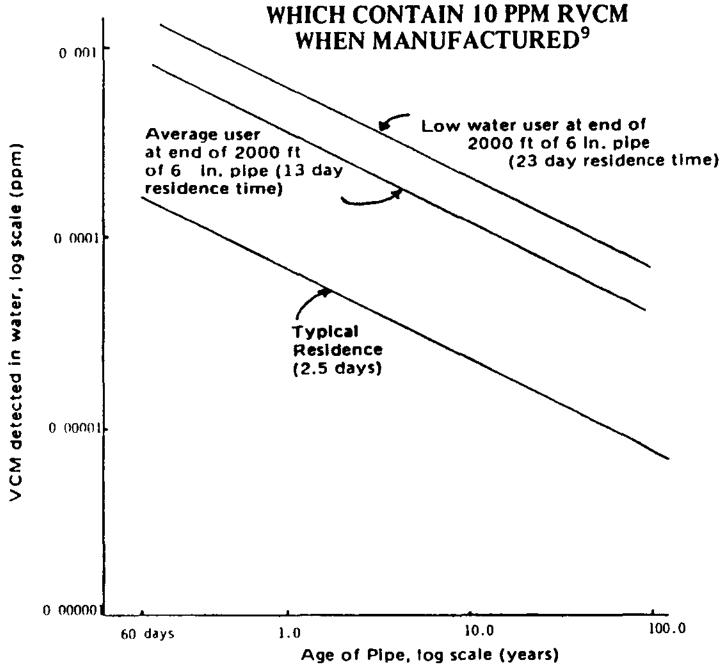
GRAPH 4

VCM CONCENTRATION IN WATER DUE TO DIFFUSION FROM PVC PIPE SYSTEMS WHICH CONTAIN 10 PPM RVCM WHEN MANUFACTURED[9]



the PVC pipe industry limiting human exposure to vinyl chloride in drinking water.

In August 1976, the NSF implemented the recommendations on RVCM limits for PVC water pipe and fittings. Since that time, manufacturers of PVC water pipe and fittings who place the NSF seal on their products have been subject to rigorous product testing and unannounced inspections by NSF to insure that PVC water pipe and fittings contain less than 10 ppm RVCM.[24] To facilitate compliance with the NSF Standard 14, most PVC pipe manufacturers require that their PVC resin be supplied with RVCM levels lower than 10 ppm. By the time the PVC resin has been processed through compounding and extrusion into PVC pipe, the cumulative, repeated application of heat in both manufacturing processes has driven off in most operations more than half of the VCM. The end effect of the self-imposed RVCM limit has resulted in an even greater factor of safety than originally considered possible.

Industry Control of RVCM in PVC Pipe. Of course, a properly managed laboratory certification program must be tough. Manufacturers who did not immediately succeed in the implementation of

TABLE 2

RVCM CONCENTRATION IN PVC RESIN[19]
(DURING JUNE, JULY, AUGUST, 1975)

PVC RESIN SUPPLIER	NUMBER OF SAMPLES ANALYZED	AVERAGE RVCM LEVEL (PPM)
R	5	3.3
S	16	59.9
T	15	14.2
U	1	3.5
V	1	5.4
W	21	12.4
X	10	97.6
Y	8	8.7
Z	7	5.7
TOTALS	84	30.2

evolution in RVCM control technology in the manufacture of PVC resin not only had impact on occupational safety in PVC pipe plants, but it also had great impact on PVC pipe product safety.

VCM MIGRATION INTO POTABLE WATER

While VCM processors, PVC resin manufacturers, and the federal government were martialing efforts to solve the problem of occupational exposure to VCM, PVC pipe manufacturers not only were seriously concerned over occupational exposure, but they were immediately concerned over product safety and consumer health. The PVC pipe industry launched a "crash" program to obtain answers to vital questions:

- How much RVCM is in PVC water pipe?
- What is a safe level of RVCM in PVC water pipe?
- How much RVCM diffuses or migrates from PVC pipe into potable water?
- What controls are necessary to safe-guard public health?

Although there was no experimental evidence regarding the carcinogenicity of VCM when ingested (as opposed to carcinogenicity when inhaled), in the interest of safety, the PVC pipe industry reacted based on the assumption that VCM could be a carcinogen when ingested. This assumption demanded an emergency reaction to determine whether or not vinyl chloride could be migrating in significant quantities into potable water conveyed in PVC pipe.

An obvious assumption was made that the level of vinyl chloride migration from PVC pipe depended upon the level of RVCM in the wall of the PVC pipe. Therefore, research and investigation was launched to determine the levels of RVCM remaining in PVC after extrusion into pipe.[5] This was no simple project. The industry first had to develop a new method of analysis sufficiently sensitive to detect minute traces of RVCM in PVC pipe. The method developed employed detection by flame-ionization gas chromatography with identification by mass spectrometry.

Vinyl Chloride Migration Basic Research. In the summer of 1975, the PVC pipe industry launched initial investigation and analysis. Table 3 presents RVCM data on pipe produced from PVC resin

TABLE 3

RVCM CONCENTRATION IN PVC PIPE SAMPLES[19]
(DURING SUMMER, 1975)

PLANT DESIGNATION	PIPE SIZE NOMINAL DIAMETER (IN.)	RVCM IN PVC RESIN (PPM)	RVCM IN PVC PIPE (PPM)	% VCM LOST
A*	3	14 or 26	4.7	82 or 66
A	6	14 or 26	2.7	90 or 81
A	8	14 or 26	2.7	90 or 81
A	10	14 or 26	2.9	89 or 79
B	2.5	8.2	2.0	76
B	2.5	8.2	3.4	59
B	2.5	8.2	2.0	76
B	1.5	8.2	3.5	57
C	6	20.3	3.4	83
C	6	20.3	3.4	83
C	6	27.7	3.5	82
C	6	27.7	2.8	86
D	3	5.0	1.9	62
D	3	5.0	2.0	60
D	3	5.0	1.7	66
D	3	5.0	1.1	78
E	4	13.1	2.3	82
E	4	13.1	5.2	60
E	4	13.1	2.8	79
E	4	13.1	1.6	88
F	3	N/A	3.2	–
F	4	N/A	2.4	–
F	8	N/A	1.7	–
AVERAGE VALUES			2.7	76

*Note: In plant A, two PVC resins were used in manufacture of pipe. Pipe could have been produced from either resin.

sophisticated landmark research based on the "worst case" assumption that VCM could be carcinogenic when ingested as a contaminant in water. The basic research in a number of laboratories, the theoretical model, and the field test site research strongly supported the assumption that RVCM in PVC water pipe has not created a significant health *hazard.*[10,21] *However, it is entirely reasonable when considering any potential hazard to human health to select a very large factor of safety.*

In keeping with this commonly accepted philosophy, the PVC pipe industry did not consider the matter closed upon completing research which clearly demonstrated little cause for concern. Although the U. S. Government did not deem it necessary to regulate RVCM in PVC pipe or to monitor or regulate the use of PVC water pipe, the industry believed strongly that additional safeguards were *necessary to increase further the factor of safety guarding consumer health.*

NSF RVCM Monitoring Program. On August 19, 1976, representatives of the PVC resin and pipe industries serving on the National Sanitation Foundation (NSF) Industry Advisory Committee recommended to the NSF that Standard 14 be revised to incorporate maximum permissible limits for RVCM in PVC potable water pipe. Nationally recognized product standards for PVC potable water pipe manufactured in North America specify that the pipe must be produced to meet the requirements defined in NSF Standard 14. The Industry Advisory Committee, working closely with the Uni-Bell Plastic Pipe Association and the Plastics Pipe Institute, recommended that "the maximum limit shall be 10 ppm Residual Vinyl Chloride Monomer" in PVC potable water pipe and fittings.

The maximum limit of 10 ppm RVCM was established based on the theoretical model for RVCM diffusion, the laboratory research, and the field test site research. A limit of ten (10) ppm RVCM was selected based on the conclusion that vinyl chloride migration from the wall of nominal one-inch diameter Schedule 40 (ASTM D 1785) PVC pipe (containing 10 ppm RVCM) into stagnant water retained in the pipe will be undetectable at a 2.0 ppb sensitivity in analysis.[22] Therefore, migration of VCM in larger diameter PVC pipes would be even lower and vastly lower yet if the PVC pipe is conveying flowing potable water.

Graph 4 predicts the potential migration of vinyl chloride into potable water conveyed by nominal 6-inch diameter pipe containing 10 ppm RVCM. The predictions are based on the theoretical model. The graph demonstrates that *even in extreme conditions where water* residence time is 23 days in a nominal 6-inch PVC pipe containing 10 ppm RVCM, any vinyl chloride present in the water should be less than one (1) ppb.[9] A huge factor of safety has been self-imposed by developed could not be verified by a mass spectrometer, the effort by USEPA was thorough and impressive. The data must be considered valuable to the overall investigation of RVCM. The lower detection limit reported by USEPA in the analysis was 30 parts per trillion (ppt). The highest concentration detected was found at the Georgetown, Texas test site. That concentration was reported to be 1.4 ppb.[10]

It is obvious that the levels of vinyl chloride detected in field test water samples were extremely low by comparison with laboratory test data. The difference is readily explained. Laboratory analysis was performed using water samples confined in a stagnant condition for substantial periods of time. The dilution which naturally occurs in a typical water distribution system is considerable. It should be noted that water demand in the Coolidge, Arizona test site was exceptionally low. USEPA data reported 0.3 ppb VCM in the water collected at that site; however, they declared the analytical results spurious in that they also detected the same concentration of VCM in the source water. In additional tests, USEPA was unable to detect VCM in that distribution system even though flow rates were extremely low.[10]

With the evolution in vinyl chloride control technology used by the PVC resin manufacturers, it is reasonable to assume that vinyl chloride migration from PVC water pipe manufactured today in North America must be substantially lower than the levels reported in the field research. R. C. Dressman and E. F. McFarren reported in their summary of the USEPA research:

> "The concentration of VC in the newest, longest system tested (Georgetown) was low compared with the level deemed hazardous to animals. Manufacturers claim that pipe made for water use within the past year has a lower free vinyl chloride content than pipe manufactured earlier. Large factors of safety therefore should be inherent in the use of the pipe."[10]

R. C. Dressman and E. F. McFarren further elaborated on the levels of vinyl chloride they detected in potable water samples:

> "These levels are well below those that thus far have been associated with adverse effects in experimental animals, and these levels should decline as lower residual monomer pipe is put into use."[10]

RVCM CONTROLS FOR PUBLIC HEALTH

The PVC industry and the U. S. Government had crossed new frontiers in trace contaminant analytical technology. The industry and the U. S. Government had conducted a substantial quantity of

with RVCM levels evaluated as shown. Twenty-three (23) PVC pipe samples, selected at random from the production of six (6) pipe plants, were analyzed as shown in Table 3. The average RVCM concentration in the PVC pipe walls was 2.7 ppm.[21] It should be noted that the heat of extrusion resulted in a substantial reduction in RVCM. It was determined that seventy-six percent (76%) average of the RVCM present in the PVC resin was driven off during extrusion of pipe.

In general, the diffusion or migration of an entrapped volatile gas from a solid material increases with increased temperature.[4,7] This represents a proper description of the process of RVCM migration from PVC.[22] Although in 1975 the average RVCM levels in PVC resin still exceeded 30 ppm, the average levels of RVCM in PVC pipe, in most instances, were less than 5 ppm.

In April 1976, the National Sanitation Foundation (NSF) initiated a major investigation to determine the level of RVCM occuring in PVC water pipe manufactured that year. The data obtained in their investigation is shown in Table 4. Two hundred and forty-six (246) PVC pipe samples obtained from 68 PVC pipe plants were analyzed for RVCM content. Eighty-nine and four-tenths percent (89.4%) of the PVC pipe samples analyzed contained RVCM at levels lower than 10 ppm.[6]

TABLE 4

RVCM CONCENTRATION IN PVC PIPE AND FITTINGS[6]
(STUDY CONDUCTED DURING APRIL, 1976)

NUMBER OF SAMPLES ANALYZED	RVCM ≤ 10 PPM		10 PPM < RVCM ≤ 20 PPM		20 PPM < RVCM ≤ 50 PPM		RVCM > 50 PPM	
	NO.	%	NO.	%	NO.	%	NO.	%
PVC Pipe—246	220	89.4	18	7.3	7	2.8	1	0.4
PVC Fittings—43	21	48.8	4	9.3	7	16.3	11	25.6

289 SAMPLES PARTICIPATED (ABOUT 15% FITTINGS)
68 PVC PIPING FABRICATOR PLANTS PARTICIPATED

Having established a clear understanding of the RVCM levels typically found in PVC water pipe manufactured in 1976, the industry's efforts then had to be directed toward research to define the "safe level" of RVCM in water pipe. This research required careful investigation of the RVCM diffusion process from a solid PVC matrix. The relationship between the level of RVCM present in a PVC pipe wall and the level of migration of vinyl chloride into water conveyed in the pipe had to be established.

A series of laboratory research projects was launched by the industry without delay to define the rate of RVCM diffusion or migration from the walls of PVC water pipe. As the protocols for these research projects were developed, the PVC industry worked closely with the U. S. Food and Drug Administration (FDA) and the U. S. Environmental Protection Agency (USEPA). Research on RVCM diffusion from PVC pipe was conducted by the following organizations:

- B. F. Goodrich Chemical Company
- Diamond Shamrock Corporation
- Ethyl Corporation
- Johns-Manville Corporation
- USEPA (Cincinnati Research Laboratory)

Tests were conducted to evaluate monomer migration from new and old PVC pipe. The effects of pipe size, temperature, water pressure and water quality variation were evaluated. Research again required the development of new analytical technology. Substantial effort and investment were dedicated to development of analytical techniques and apparatus capable of detecting the presence of vinyl chloride in water with a sensitivity as low as 2 ppb (parts per billion). To demonstrate the extremely minute level of this sensitivity to trace materials, it could be helpful to quantify 1 ppb. One part per billion represents approximately one minute taken from the entire passage of time since the Emperor Nero persecuted the early Christians in ancient Rome. Thirteen years ago when mankind had reached the level of technological advancement which made possible a voyage to the moon, scientists were inspired by the "incredible" sensitivity of "new" analytical techniques which could find traces of materials as small as 50 ppm (parts per million). This concentration is 50,000 times greater than 1 ppb (one part per billion) which can now be detected with conventional instrumentation.

It should be noted that the research on RVCM reported by USEPA was conducted with instrumentation which provided levels of sensitivity in the range of 30 parts per trillion.[2,10] USEPA used gas chromatography with a microcoulometic titration detector. Unfortunately, at the incredibly low levels of detection employed by USEPA scientists, the contaminants detected could not be conclusively labeled with accuracy by mass spectrometry.[21] However, the USEPA data is valuable.

The research results revealed that migration of vinyl chloride from a solid PVC matrix does occur and is predictable.[4,5,9] Table 5 presents data obtained in research by Johns-Manville Corporation. The vinyl chloride detected in water is reported in ppm for a pipe

field sites and tested at the Johns-Manville Research Center. With analytical technology sensitive to 2 ppb, no vinyl chloride was detected in water conveyed through PVC pipe.[19]

TABLE 9

IN-FIELD VCM WATER SURVEY[20]

COMMUNITY	AMOUNT OF PVC PIPE (FT)	SAMPLING POINT	VCM DETECTED IN THE WATER (PPM)
COOLIDGE, AZ	6280 (INSTALLED 1964)	BEGINNING OF PVC END OF PVC	NON-DETECTABLE* NON-DETECTABLE*
PIONEER, CA	81900 (INSTALLED 1966)	BEGINNING OF PVC END OF PVC	NON-DETECTABLE* NON-DETECTABLE*
ROSEBURG, OR	18480 (INSTALLED 1966-67)	BEGINNING OF PVC END OF PVC	NON-DETECTABLE* NON-DETECTABLE*
GEORGETOWN, TX	66000 (INSTALLED FEB 1975)	BEGINNING OF PVC END OF PVC	NON-DETECTABLE* NON-DETECTABLE*
SALADO, TX	2800 (INSTALLED 1969)	BEGINNING OF PVC END OF PVC	NON-DETECTABLE* NON-DETECTABLE*

*non-detectable at 0.002 ppm

Table 10 presents data obtained in analysis of duplicated water samples taken and tested by USEPA. Although the analytical data

TABLE 10

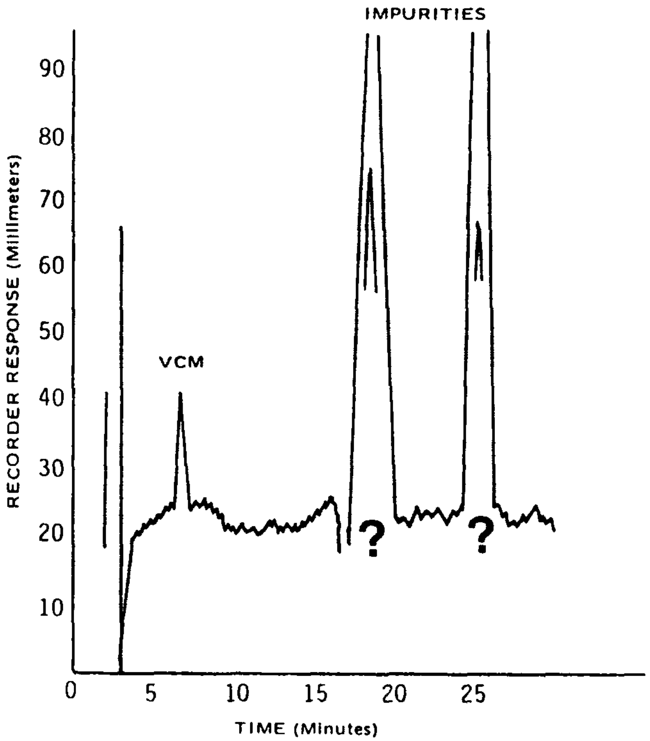
PVC PIPE SYSTEMS STUDIED[10]

Parameter	WATER UTILITY				
	Coolidge, Ariz.	George-town, Tx.	Pioneer, Calif.	Roseburg, Ore.	Salado, Tx.
Year pipe manufactured	~1964	1975	~1966	1966-67 (1 39 km, 1971)	~1968
Pipe					
Length-*km*	1.6 1.1	4.8 15	7.6 3.7	4.94 0.68	0.18 0.48 0.18
Length-*mi*	1.0 0.69	3.0 9.5	4.7 2.3	3.07 0.42	0.11 0.30 0.11
Size-*in.*	3 2	6 & 8 4 & 5	6 4	3 2	8 6 2
Total wall area-m^2	560	8200	4800	1300	370
Total wall area-*sq ft*	6000	88000	52000	14000	4000
Water temperature-*C*	~20	22-25	22-24	14	21-23
Sampling point					
Source	x			x	
Well head		x			x
Treatment plant			x		
End of pipe	x	x	x	x	x
Sampling date	8/22/75	10/10/75	9/16/75	10/17/75	10/10/75
VC concentration*- *µg/l*	0.3† 0.3†	‡ 1.4	‡ 0.06	‡ 0.03	— ‡ ‡
Sampling date	9/22/75	10/28/75	—	—	10/28/75
VC concentration*- *µg/l*	‡ ‡	‡ 1.2	—	—	— ‡ ‡

*Average of triplicate analyses, corrected for recovery efficiency
†Probably spurious
‡None detected at a detection limit of 0.03 *µg/l*

FIGURE 2

VCM IN H_2O WITH HEAVY IMPURITIES



inants can clutter or mask analysis. Figure 2 shows a typical gas chromatograph response in test of a field sample of water. In fact, several trace contaminants are extremely difficult to discern from vinyl chloride with gas chromatography. Mass spectrometry is required to identify the trace contaminant detected by the chromatograph. However, a mass spectrometer cannot analyze with practical reliability at levels of concentration lower than 2 ppb.

It should be noted that test samples at each field site were collected from water flowing through the PVC pipe and from source water prior to conveyance through PVC pipe.[10] USEPA reported vinyl chloride in the source water at one test site. Although the validity of this data has been questioned, it must be emphasized that when searching for 30 parts per trillion in analysis of trace contaminants the unexpected should be expected. Thirty (30) parts per trillion can be described as one second of time in about 1,056 years.

Assessment of VCM Migration into Potable Water. Table 9 presents the data obtained in analysis of water samples collected at the

TABLE 5

RVCM DIFFUSION FROM PVC PIPE[22]

SAMPLE	AGE OF PIPE (DAYS)	DIFFUSION PERIOD (DAYS)	RVCM IN PIPE (PPM)	VCM DETECTED IN H_2O FOR S/V = 1.0/IN. (PPM)
1	250	7	<1	$<$ 0.001
2	250	7	<1	$<$ 0.001
3	250	7	<1	$<$ 0.001
4	230	7	3.8	$<$ 0.001
5	180	7	3.9	$<$ 0.001
6	220	7	26	0.0015
7	180	7	29.2	$<$ 0.001
8	240	7	32	0.001
9	300	7	52	0.0022
10	300	7	70	0.0019
11	280	7	90	0.0038
12	300	7	101	0.0038
13	240	7	131	0.0051
14	240	7	151	0.0050
15	180	7	179	0.0063
16	270	7	294	0.0087
17	300	7	300	0.0099
18	180	7	307	0.0095
19	180	7	307	0.0099

NOTE: 0.001 ppm = 1.0 ppb

R. S. Prust Data

surface to water volume ratio (s/v) of 1.0 in^2/in^3. The data indicated that the migration of vinyl chloride from PVC pipe into water is directly proportional to the s/v ratio. A s/v ratio of 1.0 in^2/in^3 approximates the conditions offered in nominal 4 inch PVC pipe. In nominal 12 inch pipe, the s/v ratio can be approximated at 0.33. The data also indicated that the rate of monomer migration was directly proportional to time of exposure. It should be noted that the Johns-Manville testing simulated a condition wherein water is retained for seven (7) days in a PVC water main. In Johns-Manville Corporation's initial research, nineteen (19) PVC pipe samples filled with distilled water were analyzed. The data revealed two vital items of information:

- The levels of vinyl chloride detected in the water were directly proportional to levels of RVCM detected in the PVC pipe wall.[22]
- When RVCM levels in the PVC pipe wall were less than 10 ppm, migration of vinyl chloride

into the water over a period of seven days was less than 1 ppb.[20]

Table 6 presents the data on vinyl chloride migration generated in research by Diamond Shamrock Corporation. In this research nominal 1 inch diameter PVC pipe (s/v - 4.1 in^2/in^3) was tested. Again, the levels of vinyl chloride detected in stagnant water were extremely low.[1,21] It should be noted that selected samples of PVC pipe with extremely high levels (greater than 100 ppm) of RVCM were analyzed.[1]

TABLE 6

RVCM DIFFUSION FROM PVC PIPE[1]

SAMPLE	AGE OF PIPE (DAYS)	DIFFUSION PERIOD (DAYS)	RVCM IN PIPE (PPM)	VCM DETECTED IN H_2O FOR S/V = 4.1 (PPM)
1	86	1	2.5	< 0.001
2	86	1	28	< 0.001
3	111	1	179	0.0068
4	72	1	283	0.021
5	7	2	<1	< 0.001
6	7	2	14.8	0.0032
7	7	2	34.8	0.0070
8	9	2	<1	< 0.001
9	9	2	14.8	0.0026
10	9	2	34.8	0.0042
11	56	2	<1	< 0.001
12	56	2	14.8	0.0018
13	56	2	34.8	0.0066
14	99	3	2.5	< 0.001
15	95	3	28	0.0022
16	127	3	179	0.0130
17	77	3	283	0.0410
18	116	150	2.5	< 0.001
19	116	180	2.5	< 0.001

J. D. Banzer Data

Table 7 presents the data on vinyl chloride migration generated in research by B. F. Goodrich Chemical Company. This research was also conducted using nominal 1 inch diameter PVC pipe containing extremely high levels of RVCM.[5]

The correlation of data between the three research projects appeared excellent. The data generated supported the conclusion that the level of trace vinyl chloride migration from PVC pipe walls is

Field Research to Evaluate Water Systems using PVC Pipe. When considering public health significance, a sense of security is not conclusively supported by laboratory experiments and theoretical models however sophisticated. The PVC pipe industry, at this point, was prepared and had to move its research into the field. The vital question remained unanswered. Was the consuming public exposed to significant levels of vinyl chloride contaminant in potable water conveyed in PVC water pipe?

The PVC pipe industry and the USEPA worked closely in this phase of research and investigation. The vital question could be answered only through careful investigation of actual potable water distribution systems in service which conveyed water through PVC pipe. Five field sites were selected for analysis by USEPA. In cooperation with USEPA, Johns-Manville Corporation also tested replicate water samples collected at the field sites.

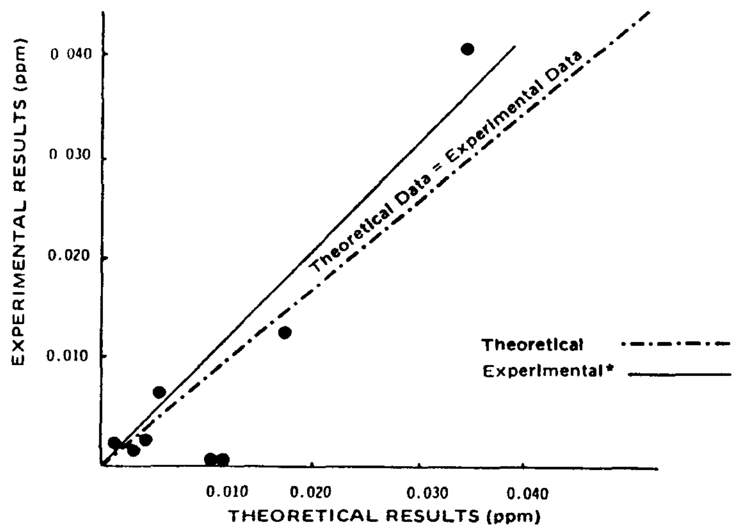
The field test sites were selected to represent relative extremes in climatic conditions. The sites were also selected because specific information was available concerning the age, length and size of the PVC pipe used.[10] The specific RVCM levels in the PVC pipe were not analyzed. However, it was established that all of the pipe installed in the distribution systems was manufactured before February 1975. It is reasonable to assume that the original RVCM concentration in the walls of the PVC pipe could vary from 10 ppm to 200 ppm.

The logistics and complications involved with this phase of the RVCM research were considerably more taxing that those experienced in the previous research conducted in controlled laboratory conditions. Vinyl chloride, as volatile gas, is elusive and difficult to analyze in water samples. The moment that the water is exposed to open atmosphere, any vinyl chloride present in the water commences diffusion out of the water into the air. Extreme caution was necessary to collect representative samples of potable water from the field sites. The water samples were collected in sealed serum reaction bottles filled without air space. The samples were then refrigerated during shipment and in the laboratory. Because heat increases the volatility of VCM, the samples were warmed to room temperature only when ready for immediate analysis.[10]

In controlled laboratory conditions, gas chromatography could provide analysis of VCM in distilled water with a sensitivity of 1 ppb and lower. However, when analyzing field water samples, a large number of trace contaminants are present and render analytical procedures vastly more complicated. In consequence, the PVC industry selected 2 parts-per-billion (2 ppb) as a reasonable detection level. USEPA used analytical procedures reported to be sensitive to about 30 parts per trillion (30 ppt);[10] however, when analyzing at these extremely low levels of sensitivity a great number of trace contam-

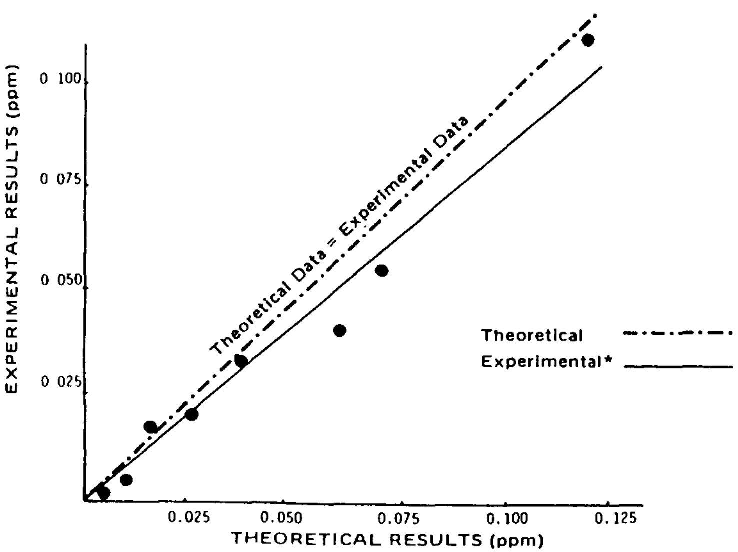
GRAPH 2

THEORETICAL VS. EXPERIMENTAL* RVCM DIFFUSION RESULTS FOR RESULTS REPORTED IN TABLE 6[22]



GRAPH 3

THEORETICAL VS. EXPERIMENTAL* RVCM DIFFUSION RESULTS FOR RESULTS REPORTED IN TABLE 7[22]



*Experimental data plotted with least squares regression

TABLE 7

RVCM DIFFUSION FROM PVC PIPE[5]

SAMPLE	AGE OF PIPE (MONTHS)	DIFFUSION PERIOD (DAYS)	RVCM IN PIPE (PPM)	VCM DETECTED IN H_2O FOR S/V = 4.1/IN. (PPM)
1	~6	3	22	0.0006
2	~6	7	22	0.0022
3	~6	14	22	0.0046
4	~6	3	177	0.0173
5	~6	7	177	0.0335
6	~6	14	177	0.056
7	~6	3	292	0.021
8	~6	7	292	0.0414
9	~6	14	292	0.113
10	~12	14	29	0.0105

A. R. Berens, G. A. Daniels Data

extremely low compared to RVCM levels in the PVC pipe walls. The data further indicated that vinyl chloride migration levels into water can be mathematically predicted with a reasonable statistical level of confidence.[21]

Theoretical Model for VCM Migration. At this point in research and investigation by the PVC industry, effort was dedicated to the development of a reliable theoretical model with which vinyl chloride migration from PVC pipe (containing RVCM) could be quantitatively predicted with acceptable accuracy.

Research conducted by the organizations listed above plus others provided extensive data which supported the following theoretical assumptions:

1. The diffusion or migration of vinyl chloride from PVC (containing RVCM) obeys Fick's First Law.[22]
2. The diffusion coefficient is independent of RVCM concentration.[22]
3. The diffusion of RVCM in the PVC pipe wall is the rate controlling step.[22]
4. The concentration of vinyl chloride in the water is negligible compared to the RVCM concentration in the pipe wall.[22]

Fick's First Law can be stated:

The amount of diffusion of a given material across a unit plane area in a unit time span is directly proportional to the concentration gradient across the plane.

Based on the above assumptions supported by research data, the following theoretical model of vinyl chloride diffusion from PVC pipe into conveyed water was developed:[21]

$$M_{H_2O} = 2SM_T\left(\frac{D}{\pi}\right)^{1/2}\left[(t+t_o)^{1/2} - t_o^{1/2}\right]$$

Where:

M_{H_2O} = Total diffused vinyl chloride into water, g

S = Pipe surface area exposed to water, cm^2

M_T = Average RVCM concentration in the PVC pipe wall, g/cm^3

D = Diffusivity of vinyl chloride in PVC, $5.7 \times 10^{-8} cm^2/day$*

t = Diffusion time period, days

t_o = Pipe age before start of diffusion time period, days

*Research by G. A. Daniels supports use of this constant.[9]

Table 8 presents actual diffusion levels compared with the levels predicted by the theoretical model. Graph 1 provides a plot of these results. Graph 2 and Graph 3 provide comparison of the Diamond Shamrock and B. F. Goodrich data respectively with theoretically predicted values. When considering the extremely minute levels of vinyl chloride being detected, the correlation between laboratory data and theoretical predictions was excellent. Research and investigation today continues to support the reasonable reliability of the theoretical model.

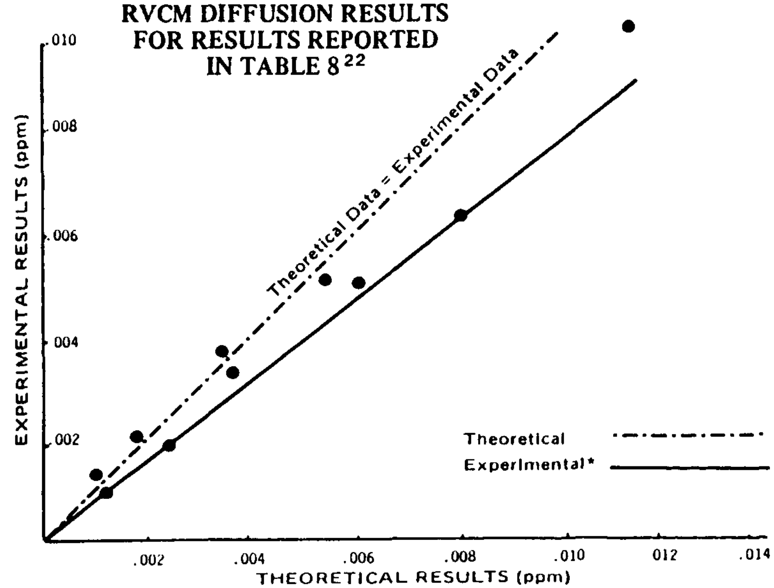
TABLE 8

EXPERIMENTAL VS. THEORETICAL RVCM DIFFUSION RESULTS[22]
VCM DETECTED IN WATER (PPM)

SAMPLE	EXPERIMENTAL	THEORETICAL
1	< 0.001	< 0.001
2	< 0.001	< 0.001
3	< 0.001	< 0.001
4	< 0.001	< 0.001
5	< 0.001	< 0.001
6	0.0015	0.0011
7	< 0.001	0.0013
8	0.0010	0.0013
9	0.0022	0.0019
10	0.0019	0.0025
11	0.0038	0.0035
12	0.0033	0.0037
13	0.0051	0.0055
14	0.0050	0.0061
15	0.0063	0.0080
16	0.0087	0.0096
17	0.0099	0.0113
18	0.0095	0.0137
19	0.0099	0.0137

R S Prust Data

GRAPH 1
THEORETICAL VS. EXPERIMENTAL
RVCM DIFFUSION RESULTS
FOR RESULTS REPORTED
IN TABLE 8[22]



*Experimental data plotted with least squares regression

1989 ADDENDUM/UPDATE TO:

"VINYL CHLORIDE; THE CONTROL OF RESIDUAL VINYL CHLORIDE MONOMER IN PVC WATER PIPE"

(UNI-TR-4)

Since this Uni-Bell technical report was last printed, i.e., 1982, the U.S. Environmental Protection Agency (EPA) has adopted national drinking-water limits for at least eight volatile organic chemicals (VOC's), including vinyl chloride. The final maximum contaminant level (MCL) for vinyl chloride was set at 2.0 parts per billion on June 24, 1987.

The level of vinyl chloride imparted to water conveyed through PVC pipes manufactured in North America is extremely low. In fact, the levels are so low that detection is usually not possible. Consequently, vinyl chloride levels, i.e., residual vinyl chloride monomer (RVCM), continues to be monitored in the pipe wall rather than the extractant water.

In North America, RVCM levels in PVC pipe materials are monitored by both the PVC resin manufacturer and the National Sanitation Foundation (NSF). The vast majority of PVC pipe manufactured in North America contain less than 1 part per million RVCM. At such low RVCM levels, it is extremely difficult to detect any vinyl chloride in the extractant water, even after long retention times. The equation provided on page 12 may be used to predict the extractant water concentration where actual measurement is not technologically possible. At the RVCM level of 1.0 part per million in the pipe wall, the predicted extractant water concentration will be less than 0.1 part per billion.

In summary, PVC pipes manufactured throughout North America provide a huge factory of safety relative to the vinyl chloride limit for drinking water. The initial vinyl chloride extractant levels are typically less than one twentieth (1/20) of EPA's allowable 2.0 parts per billion limit. Furthermore, the vinyl chloride extractant levels continually diminish with time. Thus, PVC potable water pipe can be used with confidence.

The PVC pipe industry is committed to public health and safety.

UNI-TR-4-89