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To 428
Technical Committee

December 8, 1987

Roy T. Gottesman
The Vinyl Institute
355 Lexington Avenue
New York, NY 10017

SUBJECT: PAPER ON VCM CONTAMINATION

Dear Mr. Gottesman

I met Dr. Kathleen Wolf at a recent conference on waste minimization. Subsequently, she sent me the attached reprint of her paper on VCM contamination. I thought you may be interested.

Sincerely,



Joseph C. Ledvina
Director, Environmental Activities

ajo

Attachment

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DR. R. T. GOTTESMAN

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VINYL CHLORIDE CONTAMINATION: THE HIDDEN THREAT*

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Summary

Vinyl chloride - an established human carcinogen - has been found in groundwater and in gases emitted from sanitary landfills. In many cases, the chemical itself was not placed in those locations and its origin is unknown. This paper presents and analyses a number of possible origins. The two most likely include biotransformation and chemical reaction. Biotransformation leading to a vinyl chloride end product has been observed in the laboratory. The analysis shows chemical reaction resulting in the formation of vinyl chloride might be favored in certain instances. The results suggest that further research, particularly focusing on these two routes, could shed light on the processes of vinyl chloride formation in the environment.

1. Introduction

In the last several years, vinyl chloride (VC) has been detected in the air, water, and soil in locations where the substance was not disposed of or stored. This raises questions about the origin of the VC, an established human carcinogen, about how widespread it is in the environment, and about its ultimate fate. Indeed, if the VC is being created through an environmental process, then concentrations may increase over time and human health may eventually be adversely affected.

In this paper, we explore the possible origin of the vinyl chloride. Our results suggest that there may be more than one source or mechanism of formation in land disposal sites and groundwater aquifers. The existing data are insufficient for a more rigorous analysis at the present time, and our conclusions are speculative and designed primarily to focus more attention on the question.

In what follows in Section II, we describe several locations where vinyl chloride has been found. In section III, we present production and use data that suggest the chemical was probably not used or disposed of near these sites. Its presence, however, is of concern because of potential human health effects

*Views expressed in this paper are the authors' own and are not necessarily shared by the Rand Corporation or its research sponsors.

which we also describe. In Section IV, we analyze six possible explanations of vinyl chloride's presence. These include formation through reduction by microorganisms, formation through chemical reaction, and migration of VC from various sources. In Section V, we summarize our results and make some concluding remarks.

II. Sources of vinyl chloride

VC has been found in trace amounts in the Santa Clara Valley. It was detected in the range of 50 to 500 parts per billion in the groundwater in the vicinity of three separate plants manufacturing electronics equipment [1]. Such plants use significant amounts of chlorinated solvents each year, most of which is stored in underground tanks. This so-called clean industry received a great deal of publicity in recent years when it was found that a number of the storage tanks were leaking. Because it is unlikely that these plants ever purchased VC for any purpose, its detection in the soil and groundwater in the area is curious. Another source also reports the presence of VC and groundwater in the same general area [2,3]. VC has, in fact, been found in groundwater in trace concentrations throughout the U.S. [4,5].

The chemical has also been detected in the gas collection systems and the ambient air surrounding hazardous waste disposal sites. At one such site - BKK landfill in West Covina, California - VC was detected in spite of the fact that the firm had not accepted the chemical for disposal for some time [6]. Two separate industry sources indicate that VC has also been detected at the perimeter of sanitary landfills where only municipal trash was buried and where disposal of VC was never permitted.

III. Background data on vinyl chloride

Production and use

In 1984, production of VC - called VC monomer - amounted to somewhat more than 6 billion pounds or about 2.7 million metric tons. VC is produced by eight manufacturers in eleven domestic plants. Virtually all of the VC produced today is used as an intermediate in the manufacture of polyvinyl chloride (PVC) or other copolymers [7]. PVC is today used in a variety of products throughout the economy including piping, tubing, flooring, textiles, coating, wire, cable, film, photograph records, and bottles [8].

Prior to 1974, VC was used as an aerosol propellant in a variety of products such as pesticides, drugs, and cosmetics. Although manufacturers may have actually stopped using VC for this purpose for financial reasons, in 1974 three government agencies - the Food and Drug Administration (FDA), the Environmental Protection Agency (EPA), and the Consumer Product Safety Com-

mission (CPSC) - banned VC's use in self-pressurized aerosols for household use [9,10].

Health effects

The ban on use of VC in aerosol applications in 1974 was prompted by indisputable evidence that VC was a human carcinogen. At that time, Goodrich, a VC and PVC producer, announced that four of its workers had died of angiosarcoma, a rare liver cancer. By the spring of 1968, 68 cases of the disease had been reported [10]. The highest incidence appeared in workers who cleaned the polymerization reactor where concentrations of VC averaged between 250 and 300 parts per million (ppm) and peak concentrations were as high as several parts per thousands.

The results of animal studies confirm the unequivocal carcinogenicity of VC. In 1974, an Italian group reported that rats had developed angiosarcoma in inhalation studies with VC concentrations at 250 ppm [11]. Another experiment conducted in 1975 reported angiosarcoma at 50 ppm [12]. Since then, other studies have verified that VC is a carcinogen through inhalation and ingestion [13].

There is today a consensus that VC is carcinogenic. The National Toxicology Program lists it as one of the few dozen chemicals that are established human carcinogens [14]. Its identification in groundwater and at the perimeters land disposal sites therefore is cause for concern.

IV. Vinyl chloride origins

In what follows, we discuss several possible processes that could result in VC's presence in inexplicable locations. These include anaerobic microbial transformation, chemical transformation, PVC outgassing, PVC depolymerization, emission from aerosol cans, and solvent contamination. We examine the first two - biotransformation and chemical transformation - in some detail and only briefly discuss the other processes.

By way of introduction, we first describe several chemicals that are widely used, disposed of in hazardous waste landfills, and stored in underground storage tanks. Such chemicals include the industrial solvents 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), and perchloroethylene (PERC). Annual historical production of these chemicals is presented by Wolf and Chesnutt [15] and reproduced here in Table 1 for 1984.

The values of Table 1 show that the combined annual production of the three industrial solvents is huge - 760 thousand metric tons. They are used in a variety of applications including the dry cleaning and metal cleaning industries. They are stored in underground tanks near businesses across the U.S. and are present in hazardous waste land disposal sites all over the nation. In

TABLE 1

Production of chlorinated solvents - 1984

Solvent	Production (thousand metric tons)
TCA	306
TCE	200
PERC	260

Source: U.S. ITC [16]; CMR [17].

the discussion of VC origins that follows, we will refer to these chemicals frequently.

Biotransformation

Three investigators have presented evidence that under the anaerobic condition that exists in groundwater, certain chlorinated hydrocarbons are biodegraded. For reference, we show the degradation sequence in Fig. 1.

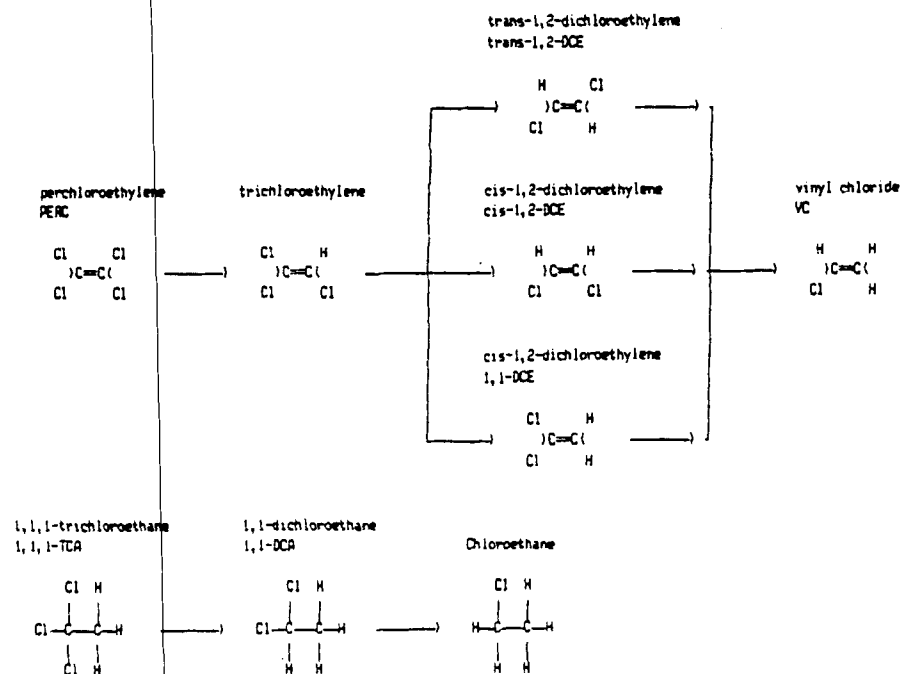


Fig. 1. Possible biodegradation sequence.

TABLE 2

Biodegradation half-lives

Chemical	Half-life (days)
PERC	34
TCE	43
1,1-DCE	53
<i>cis</i> -1,2-DCE	long*
<i>trans</i> -1,1-DCE	long*
VC	long*
1,1,1-TCA	16
1,1-DCA	long*
Chloroethane	10

Source: Wood et al. [5].

*Long means no detectable reduction of the chemical over 30 to 60 days.

The biotransformation steps each result in the replacement of a chlorine atom in the molecule by a hydrogen atom. In the top sequence, a chloride atom in PERC is replaced with a hydrogen atom, transforming it to TCE. In the next step, substitution of one chlorine atom by a hydrogen atom in TCE can, in principle, lead to the three products, *cis*- and *trans*-1,2-dichloroethylene (*cis*-1,2-DCE and *trans*-1,2-DCE) and 1,1-dichloroethylene (1,1-DCE). In the third step, replacement of the third chlorine atom with a hydrogen atom produces the compound of interest - VC. In the bottom sequence, TCA is first converted to 1,1-dichloroethane (DCA) which is converted, in turn, to chloroethane.

In one study, Wood et al. [5] identified VC, the three DCEs, 1,1-DCA, and chloroethane in an aquifer that supplies drinking water. The authors stress that these chemicals have no logical source since they are not produced or in wide use today.* The investigators isolated and cultured anaerobic bacteria from groundwater and muck-water in the laboratory in the presence of PERC. From these experiments, the authors determined the biodegradation half-lives of the chemicals shown in Table 2. In both the current work and the earlier work, Wood et al. [5] found that the ratio of production of *cis*-1,2-DCE to *trans*-1,1-DCE was at least 25 to one.

Wood et al. [5] also examined a series of actual spills. In one such spill which occurred 15 years ago, concentrations of TCE, TCA, and PERC - the commonly used solvents - were still extremely high. In samples of water deeper in the aquifer or farther downstream from the spill site, concentrations of these

*As discussed earlier in Section II, VC monomer is, in fact, produced in huge quantities. It is true, however, that virtually all of it is converted into PVC.

TABLE 3

Chemical concentrations

Sample	Chemical (g/l)					
	PERC	TCE	1,1-DCE*	cis-1,2-DCE	trans-1,2-DCE	VC
PERC	1,630	30	2	^b	^b	1
Muck before incubation	1,430	18	^c	^c	^c	^c
Muck after 21-day incubation	466	78	2.5	63.3	1.8	28.3
Groundwater-treatment plant	0.02 ± 0.03	0.29 ± 0.14	0.21 ± 0.21	25.6 ± 3.4	1.6 ± 0.4	6.8 ± 6.0
Groundwater-spill site	^b	426 ± 45.7	0.68 ± 0.16	1145 ± 302	4.9 ± 2.4	82.1 ± 21.5

Source: Parsons et al. [18].

*The authors call this dichloromethane. See footnote in text for explanation.

^bLess than detection limit of 0.5 g/l.^cNot measurable.

chemicals were lower and concentrations of their transformation products were higher.

A second group - Parsons et al. [18] - found VC and *cis*- and *trans*-1,2-DCE in the groundwater in Southern Florida where local industries do not use the chemicals. Using water with indigenous microorganisms injected with PERC in the laboratory, the group demonstrated the formation of TCE and the other chemicals measured using gas chromatography* (GC) in muck but not in autoclaved muck - the control. The results are summarized in Table 3.

In the third sample - the muck after the 21 day incubation - Parsons et al. [18] found a PERC concentration of 466 µg/l, a fairly high concentration of TCE (78 µg/l, reasonable concentrations of the next sequence of compounds, 1,1-DCE and *cis*- and *trans*-1,2-DCE (67.6 µg/l combined), and a smaller concentration of VC (28.3 µg/l). These data are certainly suggestive of the chain of successive reduction in Fig. 1. Note also that the Parson et al. [18] data agree with Wood et al. [5] in that *cis*-1,2-DCE formation is much favored over *trans*-1,2-DCE formation. Furthermore, the data of Table 3 also suggest even less of a tendency to form 1,1-DCE.

The information in Table 3 on the actual groundwater measurements are also persuasive. At this site in question, TCE and not PERC was spilled and detected. Although the authors do not refer to the length of time since the spill, the high indicated conversions - especially to *cis*-1,2-DCE suggest it probably occurred years ago.

McCarty [19] reports the formation of DCE and VC from PERC and TCE

*The authors also mention that they found either dichloromethane (CH₂Cl₂) or 1,1-dichloroethylene (1,1-DCE) but that the GC could not distinguish between them. With reference to Fig. 1, it is not likely that a one-carbon chemical like methylene chloride (dichloromethane) would be present. The presence of 1,1-DCE, on the other hand, would be expected - and it is clear this chemical was found.

in unpublished experiments conducted in his laboratory. Under anaerobic conditions, TCA and PERC were almost completely transformed. In contrast under aerobic conditions, no biotransformation was detected. McCarty also states that the evidence suggests that VC would in turn be degraded into carbon dioxide.

All three groups mention that bacteria might be used to decontaminate groundwater polluted by spills of solvents like PERC and TCE. It is worth noting here that the process of VC degradation to carbon dioxide and presumably HCl, requires further investigation. This step may not occur at all, or it may be extremely slow. In this light, one study reports that over the 17-day experimental period, the VC concentration remained virtually constant [4]. If degradation was not significant, the technique would not be safe. We would be faced with a situation where biodegradation of toxic animal carcinogens - PERC and TCE - leads to production of a more dangerous substance, VC - an established human carcinogen.

Chemical transformation

A second potential origin for the VC found in groundwater and soil is formation through chemical reaction. One possibility is hydrolysis of the commonly used solvents with water or base substitution of chlorine. This reaction would be more favored in a basic rather than an acidic environment and would result in the formation of products containing oxygen - not in products like DCE or VC. Since these products have not been identified, the reaction is probably not favored. Indeed, there is evidence that hydrolysis of the three solvents is very slow [20].

A second possibility is that the VC and DCE found at various sites could be formed by a chemical reaction that removes both a chlorine and hydrogen atom (dehydrochlorination). The top two reactions depicted in Fig. 2 show how VC can be formed through dehydrochlorination of two different starting products - 1,1-DCA and 1,2-DCA. Figure 3 shows four separate dehydrochlorination reactions that can lead to the formation of the three DCEs. The two starting chemicals in this case are 1,1,1-TCA and 1,1,2-TCA.

A third possibility is that VC is formed through a dechlorination reaction in which a chlorine molecule is removed. This process is depicted in the two bottom reactions in Fig. 2 which show formation of VC through dechlorination of 1,1,1-TCA and 1,1,2-TCA. There are similar reactions for the formation of DCE from dechlorination of ethanes containing four chlorine atoms. Such chemicals are not widely used, however, except as intermediates and for simplicity, we do not examine them further.

In the Santa Clara Valley, the chemicals appearing in Figs. 2 and 3 were found in the groundwater and in the soil near many firms in the area at the concentrations indicated in Table 4 [1]. In reference to the table, recall that VC can be formed from DCA or TCA and that DCE can be formed from TCA.

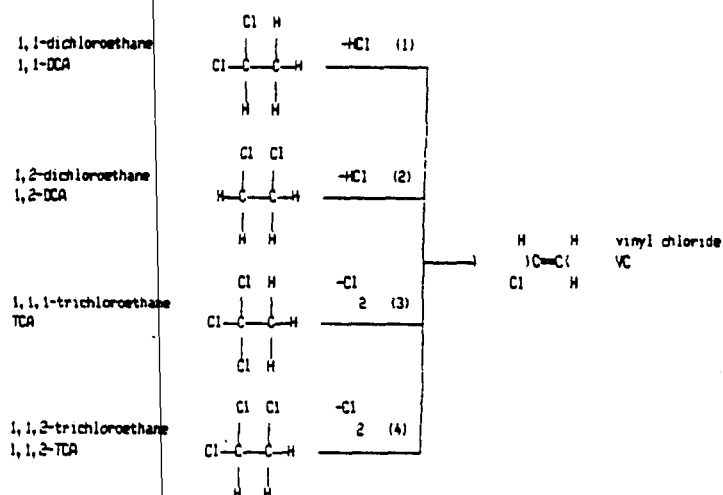


Fig. 2. Paths for VC formation.

At the Ford Motor Co., the VC found in the groundwater could have been formed either from dehydrochlorination of DCA or dechlorination of 1,1,1-TCA. DCA, like VC was found in the groundwater whereas 1,1,1-TCA was found only in the soil. The *trans*-1,2-DCE found at the site could not have been

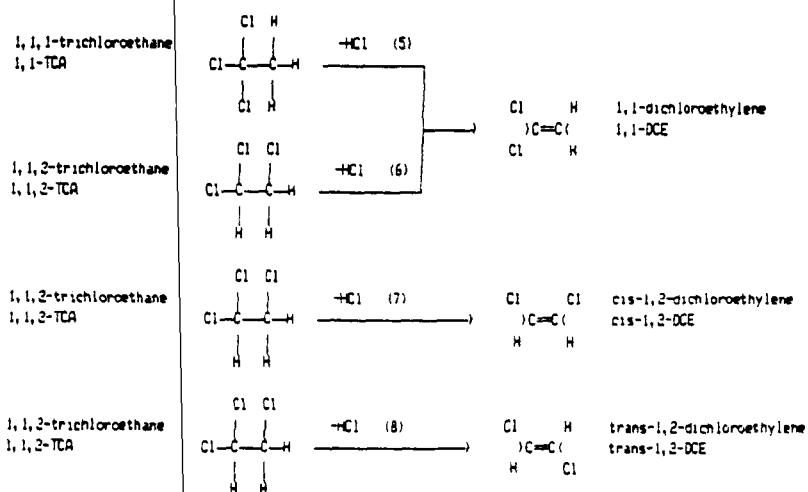


Fig. 3. Paths for DCE formation.

TABLE 4

Contamination levels at sites in the Santa Clara Valley

Site	Chemical	Concentration (ppb)	
		Groundwater	Soil
Ford Motor Corp - Milpitas	DCA ^a	< 100	
	<i>trans</i> -1,2-DCE	50 to 100	
	1,1,1-TCA		< 100
	VC	50 to 100	
Great Western Chem. Co. - Milpitas	DCA ^a	> 1000	
	1,1-DCA	100 to 500	
	DCE ^b	> 1000	< 100
	1,1-DCE		> 1000
	1,1,1-TCA		> 1000
Intel Corp. - Mountain View	DCA ^a	< 100	
	DCE ^b	100 to 500	
	<i>trans</i> -1,2-DCE	> 1000	< 100
	1,1,1-TCA	100 to 500	
	VC	100 to 500	
Sunnyvale Intersil	1,1-DCE	< 100	
	<i>trans</i> -1,2-DCE	> 1000	
	1,1,1-TCA		< 100
	VC	< 100	

Source: White Paper [1].

^aNot specified if this chemical is 1,1-DCA or 1,2-DCA.^bNot specified if this chemical is 1,1-DCE or 1,2-DCE.

formed from either DCA by dehydrogenation or 1,1,1-TCA by transformation to 1,1,2-TCA and subsequent dehydrochlorination (see Fig. 3).

At the Great Western Chemical Co., no VC was identified. An unspecified DCE and 1,1-DCE were found at concentrations greater than 1,000 parts per billion (ppb) in the groundwater and soil, respectively. The only product detected that could lead to the formation of the DCEs is 1,1,1-TCA which was measured only in the soil at a concentration greater than 1,000 ppb.

The chemicals found near the Intel Corp. site include DCE, DCA, VC, and 1,1,1-TCA. VC, found at 100 to 500 ppb in the groundwater, could have been formed from the dehydrochlorination of DCA, detected at less than 100 ppb, or from the dechlorination of 1,1,1-TCA, found at between 100 and 500 ppb. The *trans*-1,2-DCE could not have been formed from the detected products without transformation of 1,1,1-TCA to 1,1,2-TCA occurring first. The unspecified DCE, found in the groundwater at between 100 to 500 ppb is prob-

ably 1,1-DCA which could have been formed from the dehydrochlorination of 1,1,1-TCA found at the same concentration.

At the Intersil site, the VC detected in the groundwater at a concentration less than 100 ppb, could have been formed through dechlorination of 1,1,1-TCA found in the soil. The *trans*-1,2-DCE could not be formed directly from 1,1,1-TCA but the 1,1-DCE could - through dehydrochlorination.

The fact that the correct combinations of the chlorinated chemicals were found together at various sites suggests that the chemical reactions in Figs. 2 and 3 could be taking place. However, it is true as well that TCE was also found at each of the four sites. This supports the possibility that biotransformation of TCE may actually be the mechanism leading to formation of 1,1-DCE and ultimately VC as described in Fig. 1.

To investigate further the likelihood that chemical reaction may be the mechanism of origin, we calculated the enthalpy of the reactions in Figs. 2 and 3. In each case, we determined the enthalpy of formation for each species in the reaction and the enthalpy for the reaction as a whole. Table 5 displays these data. It should be noted that this thermodynamic analysis does not indicate how long it takes for a product to be formed or detected.

In the last column of Table 5, a positive enthalpy value indicates that the theoretical reaction pathway is endothermic - that it requires energy to take place; a negative enthalpy value indicates that the reaction is exothermic - that it could occur spontaneously assuming there are no kinetic or entropic barriers. The more negative is the enthalpy, the more likely the reaction will occur. From the values, we observe that none of the reactions involving VC formation is favored. In fact, the enthalpies of reaction are quite high. At the same time, we note that the reactions involving aqueous rather than gaseous HCl are favored (less positive enthalpy of reaction) and that dehydrochlorination is favored over dechlorination. The reactants in reaction numbers 1 and 2 - 1,1-DCA and 1,2-DCA - are undoubtedly in the liquid state in the environment. Because we have no data on liquid enthalpies, we present only the enthalpies of the gaseous state. We can surmise from the other table entries, however, that the enthalpies of the total reaction would be more positive or even less favored if the reactants were in the liquid state. We also note that in the environment, the HCl is likely to be in aqueous form. Those reactions where this is the case are favored over those where HCl is a gas.

Some of the reactions in Table 5 that lead to the formation of one of the DCE products could occur spontaneously. These reactions are presented in more detail in the tables of the Appendix. As we discussed above, in the environment, the reactant and product both are likely to be in liquid form and the HCl is probably aqueous. Under these circumstances, the enthalpy of the reaction that forms 1,1-DCE is -3.32 kcal/mol (see last number in column under 1,1-DCE in Table A-3 of the Appendix); that forms *cis*-1,2-DCE is -4.02 kcal/mol (see last number in column under *cis*-1,2-DCE in Table A-4 of the

TABLE 5

Enthalpy values for chemical transformation

Reaction number ^a	Enthalpy (kcal/mol) ^b	Reaction									
		1,1-DCA	1,2-DCA	1,1,1-TCA ^c	1,1,2-TCA	HCl	Cl ₂	VC	1,1-DCE	cis-1,2-DCE	trans-1,2-DCE
1	-36.4 (g)	—	—	—	—	-22.09 (g)	—	8.4 (g)	—	—	22.71
2	—	-39.7 (g)	—	—	—	-22.09 (g)	—	8.4 (g)	—	—	4.78
3	—	—	-33.1 (g)	—	—	-40.02 (aq)	0	8.4 (g)	—	—	26.01
4	—	—	-42.7 (l)	—	—	—	0	—	—	—	8.08
5	—	—	—	-33.1 (g)	—	-33.1 (g)	0	8.4 (g)	—	—	41.5
6	—	—	-42.7 (l)	—	—	-42.7 (l)	0	—	—	—	51.1
7	—	—	—	-33.1 (g)	—	-40.02 (aq)	—	—	—	—	51.1
8	—	—	—	-42.7 (l)	—	-40.02 (aq)	—	—	—	—	51.1

^aAll enthalpies are given at standard temperature and pressure.^bSee Figs. 2 and 3.^cWe approximate the enthalpy values for 1,1,1-TCA by using those of 1,1,2-TCA. Note that this approximation is probably reasonable because values for 1,1-DCA and 1,2-DCA are close to one another as are the values of 1,1-DCA and 1,2-DCE.^dThe range in values arises because there are eight combinations depending on the chemical state. See the Appendix for detailed results.

Notes: (g) indicates an ideal gas at 298°C and 760 mm pressure; (l) indicates a pure liquid at 298°C; (aq) indicates an aqueous solution. Positive enthalpies indicate endothermic reactions and negative enthalpies indicate exothermic reactions. Thermodynamic constants were obtained from Stull et al. [21].

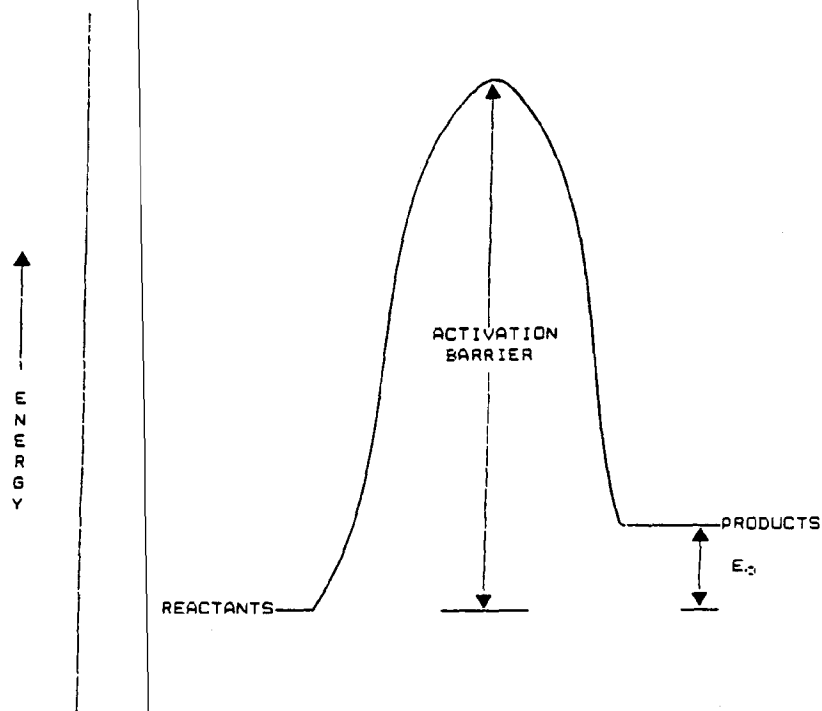


Fig. 4. Hypothetical activation barrier.

Appendix); and that forms *trans*-1,2-DCE is -3.42 kcal/mol (see last number in column under *trans*-1,2-DCE in Table A-4 of Appendix A). These values are all slightly negative suggesting the reactions could occur spontaneously.

The complete range of enthalpies involving the chemicals listed in Table 5 are given in the Appendix. We also include the enthalpies for dehydrochlorination and dechlorination of VC and DCE respectively that lead to the formation of acetylene and ethylene. It is notable that none of these second tier reactions could occur spontaneously.

The speed with which reactants form products cannot be deduced from the reaction enthalpy. Another factor that can influence the formation of products is the kinetic quantity - the activation energy barrier*. A pictorial representation of such a barrier is shown in Fig. 4. In this particular situation, the energy of the products is greater than the energy of the reactants indicating a net energy requirement. The products are higher in energy than the reactants

*Reaction rates are proportional to reaction rate constants which are inversely proportional to the exponential of the activation energy.

by only a small amount - E_0 in Fig. 4. To get the reaction to move in the direction of the products, however, a much higher energy, one equal in magnitude to the activation energy, is necessary.

The fact that a reaction theoretically could occur spontaneously according to its enthalpy value may not imply that the reaction occurs in practice. If the particular reaction has a high activation barrier, it will probably not occur. No data on the activation barrier for reaction 1 in Fig. 2 appear to be available. Although reaction 2 in Fig. 2 has been studied [22,23], no value for the height of the barrier has been established.

Data on the barriers for reaction 3 in Fig. 2 and reaction 5 in Fig. 3 involving 1,1,1-TCA are available. The height of the activation barriers for the dehydrochlorination reaction, number 5, is 54 kcal greater than the enthalpy of the reactant - 1,1,1-TCA. The barrier for the dechlorination reaction, number 3, is even higher, at an estimated 92 kcal. This suggests that significant additional energy would be required for the reactions to take place. Although we have no information on the barrier height of reactions involving 1,1,2-TCA, we doubt that it would be significantly lower than that of 1,1,1-TCA.

Factors that may favor the reactions include the presence of catalyzing agents like the microorganisms and high temperatures. Indeed, the high temperatures found in landfills result from anaerobic biodegradation processes of thermophile bacteria which flourish at 120-140°F (49-60°C). Bacterial catalysis could lower the activation energy so that detectable amounts of product would be formed. Thus, even with high activation barriers, we cannot rule out chemical reaction as the mechanism for transformation.

Migration from PVC

A third possible origin of VC is its migration from PVC - the so-called "Milk Carton Theory." In sanitary landfills, PVC in numerous forms would be expected to be present. These would include food packaging, bottles, and discarded piping and siding. Near leaking underground storage tanks, it is less obvious that PVC would be present. PVC pipe, however, has been used in water distribution systems all over the country and could be the origin of the VC found in Santa Clara Valley.

In polyvinyl chloride products, some vinyl chloride is retained within the network of the polymer as a residue from the polymerization reaction. This residue may eventually leave the polymerized material by volatilization or migration. One group has been studying VC migration in PVC pipe containing 29.5 ppm of VC [25]. When they prevented volatilization and increased the surface area of the pipe wall in contact with the water, they found that VC migrated into water at levels greater than 50 ppm. With chlorine present in the water, the VC reacted to yield products containing oxygen like chloroacetaldehyde and chloroacetic acid.

In groundwater or under soil, only small amount of volatilization from PVC

products might be expected to occur. But under normal circumstances, we might expect VC to migrate mainly into the surrounding media. Ando and Sayato [25] investigated pipes which are rigid and had reasonably thick walls. Significant migration from other types of pipe with thermal walls might be possible. In landfills, where more flexible PVC products may have been placed, VC migration would probably be lower [10].

Depolymerization of PVC

Under certain conditions the PVC can decompose to form VC molecule. In general, this requires either significant thermal energy or ultraviolet irradiation. It is unlikely that the high temperature required could be achieved or that sunlight would penetrate at sanitary landfills or groundwater.

Disposal of aerosol cans

As mentioned in an earlier section, the use of VC as a propellant in aerosol consumer products was banned in 1974. Before that time, aerosol cans containing a "heel" of VC were probably widely disposed of in sanitary landfills across the country. The VC would eventually leak from the cans as they are crushed or corrode and it would be detected in the gas collection system. Although this source of VC may adequately explain detection of the chemical at sanitary landfills, it does not explain detection of VC near underground storage tanks or in aquifers located near chemical spills. It also does not explain the origin of the DCE detected in either location.

Contamination of solvents

One other potential source of the VC is as a contaminant from the production process of chlorinated solvents. Under such circumstances, we would expect to detect small amounts of VC and, perhaps, DCE, as well, in much larger amounts of the solvents in the environment. The data of Table 4 do not allow us to draw a definitive conclusion.

Some TCA is produced from VC, and the distillation vent gas from a model plant contains 0.1 percent of VC by weight. The gas from a drying column vent in a plant producing PERC and TCE contains 21 and 16 percent of VC and 1,1-DCE by weight, respectively [26]. These data suggest that VC and 1,1-DCE may be present in small amounts in virgin TCA, PERC, and TCE when they are sold.

Because of a lack of specific information on the concentrations of all species present at landfills and at spill sites, it is not possible to decide whether the detected VC and 1,1-DCE are simply contaminants in the widely used solvents. Such data could help shed light on the VC origin.

V. Results and conclusions

Vinyl chloride and dichloroethylene have been found at sites where the widely used chlorinated solvents - TCA, PERC, and TCE - have been released into

the soil and groundwater. Vinyl chloride has also been detected in the gas streams emitted from sanitary landfills. Both vinyl chloride and dichloroethylene are used only as intermediates in the production of other chemicals so it is unlikely that either chemical was disposed of or used in the vicinity of the sites of detection.

A number of investigators have demonstrated that VC and DCE are formed in the laboratory through anaerobic transformation of TCE or PERC by microorganisms. This mechanism is a possible explanation for the origin of VC and DCE. More research is required for verification of this formation mechanism.

Our analysis suggests that another pathway - chemical reaction - may also be responsible for the formation of VC and DCE. In this case, the reactants that are converted to VC and DCE through dehydrochlorination and dechlorination include DCA and TCA. Although DCA's primary use is as an intermediate in chemical production processes, TCA is a widely used solvent. The results show that the formation of DCE is more favorable than that of VC. More research is necessary to determine whether or not this pathway is likely.

Another possible explanation for the presence of VC and DCE are that they exist as contaminants in chlorinated solvents. VC may also be present because of migration from various plastic products, depolymerization of those same products, or leakage from aerosol cans.

The intent of this paper was not to assign a definitive source to the hazardous chemicals. Its purpose, rather, was to propose a range of possible sources as the starting point for more detailed investigation. In the future, it will become increasingly important to verify the sources - particularly of VC, an established human carcinogen. As time passes, more VC may be formed, and the air and groundwater will become increasingly polluted. If we can identify the origin, we can hope to prevent or limit its formation with more certainty.

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Enthalpy of formation of vinyl chloride (VC) from 1,1-dichloroethane (1,1-DCA) at standard temperature and pressure from standard enthalpies of formation	ΔH_1 kcal/mol (STP)	Dechlorination	ΔH_2 kcal/mol (STP)	$\Delta H_{1,2}$
1,1-DCA	-10.0			
VC	-12.5			
1,1-DCA + VC	-22.5			
1,1-DCA + VC + H ₂	-10.0			
1,1-DCA + VC + H ₂ + Cl ₂	0.0			
1,1-DCA + VC + H ₂ + Cl ₂ + H ₂ O	-18.0			
1,1-DCA + VC + H ₂ + Cl ₂ + H ₂ O + H ₂	-10.0			
1,1-DCA + VC + H ₂ + Cl ₂ + H ₂ O + H ₂ + H ₂	0.0			
1,1-DCA + VC + H ₂ + Cl ₂ + H ₂ O + H ₂ + H ₂ + H ₂	0.0			
1,1-DCA + VC + H ₂ + Cl ₂ + H ₂ O + H ₂ + H ₂ + H ₂ + H ₂	0.0			
1,1-DCA + VC + H ₂ + Cl ₂ + H ₂ O + H ₂ + H ₂ + H ₂ + H ₂ + H ₂	0.0			
1,1-DCA + VC + H ₂ + Cl ₂ + H ₂ O + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂	0.0			
1,1-DCA + VC + H ₂ + Cl ₂ + H ₂ O + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂	0.0			
1,1-DCA + VC + H ₂ + Cl ₂ + H ₂ O + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂	0.0			
1,1-DCA + VC + H ₂ + Cl ₂ + H ₂ O + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂	0.0			
1,1-DCA + VC + H ₂ + Cl ₂ + H ₂ O + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂	0.0			
1,1-DCA + VC + H ₂ + Cl ₂ + H ₂ O + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂	0.0			
1,1-DCA + VC + H ₂ + Cl ₂ + H ₂ O + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂	0.0			
1,1-DCA + VC + H ₂ + Cl ₂ + H ₂ O + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂	0.0			
1,1-DCA + VC + H ₂ + Cl ₂ + H ₂ O + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂	0.0			
1,1-DCA + VC + H ₂ + Cl ₂ + H ₂ O + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂	0.0			
1,1-DCA + VC + H ₂ + Cl ₂ + H ₂ O + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂	0.0			
1,1-DCA + VC + H ₂ + Cl ₂ + H ₂ O + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂	0.0			
1,1-DCA + VC + H ₂ + Cl ₂ + H ₂ O + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂	0.0			
1,1-DCA + VC + H ₂ + Cl ₂ + H ₂ O + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂ + H ₂	0.0			
1,1-DCA + VC + H ₂ + Cl ₂ + H ₂ O + H ₂	0.0			
1,1-DCA + VC + H ₂ + Cl ₂ + H ₂ O + H ₂	0.0			
1,1-DCA + VC + H ₂ + Cl ₂ + H ₂ O + H ₂ + H ₂ + H				

1,1-DCA 1,1-dichloromethane	vinyl chloride chloroethylene	acetylene ethyne
$\begin{array}{c} \text{Cl} \quad \text{H} \\ \quad \\ \text{Cl}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{Cl}-\text{C}=\text{C}-\text{H} \\ \\ \text{H} \end{array}$	$\text{H}-\text{C}\equiv\text{C}-\text{H}$
b.p. (°C, 760 mmHg): ΔH_f°	-13.37 8.4 (g) -22.09 (g) -40.02 (aq)	-84.0 54.19 (g) 23.7 5.77
		ethylene
		$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}=\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$
	-Cl ₂ 0 (g)	-88.63 12.50 (g)
		48.9

Notes: (1) Unless otherwise specified all thermodynamic constants were obtained from Stull et al. [21]; (2) positive enthalpies indicate endothermic reactions and negative enthalpies, exothermic; (3) Abbreviations: (g) ideal gas state at 298°C and 760 mmHg pressure; (l) pure liquid at 298°C; (aq) aqueous solution; $\Delta H_{f,2,12}$ reaction enthalpies.

TABLE A-2

Enthalpy of formation of vinyl chloride (VC) from 1,2-dichloroethane (1,2-DCA) at standard temperature and pressure from standard enthalpies of formation		ΔH_1 kcal/mol (STP)		Dechlorination		ΔH_2 kcal/mol (STP)	ΔH_{12}
1,2-DCA		vinyl chloride		acetylene			
1,2-dichloromethane		chloroethylene		ethyne			
ethylene dichloride							
$\begin{array}{c} \text{Cl} \quad \text{Cl} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$		$\begin{array}{c} \text{Cl} \quad \text{H} \\ \quad / \quad \backslash \\ \text{H}-\text{C}-\text{C}=\text{C}-\text{H} \\ \quad \backslash \quad / \\ \text{H} \quad \text{H} \end{array}$		$\begin{array}{c} \text{H}-\text{C}\equiv\text{C}-\text{H} \end{array}$			
$\begin{array}{c} \text{Cl} \quad \text{Cl} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$		$\begin{array}{c} \text{Cl} \quad \text{H} \\ \quad / \quad \backslash \\ \text{H}-\text{C}-\text{C}=\text{C}-\text{H} \\ \quad \backslash \quad / \\ \text{H} \quad \text{H} \end{array}$		$\begin{array}{c} \text{H}-\text{C}\equiv\text{C}-\text{H} \end{array}$			
b.p. (°C, 760 mmHg):		83.47		-84.0			
ΔH_f°		-39.7 (g)		-22.09 (g)		23.7	
		-22.09 (g)		-40.02 (aq)		5.77	
		-40.02 (aq)		-Cl ₂		13.85	
				ethyne			
				$\begin{array}{c} \text{H} \quad \text{H} \\ \backslash \quad / \\ \text{C}-\text{C}-\text{H} \\ / \quad \backslash \\ \text{H} \quad \text{H} \end{array}$			
b.p. (°C, 760 mmHg):		-88.63		0 (g)		52.2	
ΔH_f°		12.50 (g)					

Notes: see notes of Table A-1.

Appendix

In this Appendix, we show the complete details of our enthalpy calculations. All calculations were performed according to the relationship:

$$\Delta H_{\text{REAC}} = \sum \Delta H_{\text{PRODUCTS}} - \sum \Delta H_{\text{REACTANTS}} \quad (\text{A-1})$$

Table A-1 describes the enthalpy relationships in the dehydrochlorination of 1,1-DCA to form VC. We also show the enthalpies for the second stage reactions that form acetylene and ethylene.

The enthalpies for the formation of VC from 1,2-DCA are shown in Table A-2. We again present enthalpies for the second stage reactions leading to acetylene and ethylene.

In Table A-3, we show the enthalpy relationships for conversion of 1,1,1-TCA to 1,1-DCE and VC. We also show similar data for the further conversion to acetylene.

TABLE A-3

Enthalpy of formation of vinyl chloride (VC) from 1,1,1-trichloroethane (1,1,1-TCA) at standard temperature and pressure from standard enthalpies of formation		ΔH_f kcal/mol (STP)	Dechlorination	ΔH_f kcal/mol (STP)	$9\Delta H_{12}$
1,1,1-TCA 1,1,1-trichloroethane methyl chloroform	1,1-DCE 1,1-dichloroethylene vinylidene chloride			acetylene ethyne	
$\begin{array}{c} \text{Cl} \quad \text{H} \\ \quad \\ \text{Cl}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{Cl} \quad \text{H} \end{array}$	$\begin{array}{c} \text{Cl} \quad \text{H} \\ \quad \\ \text{Cl}-\text{C}=\text{C}-\text{H} \\ \quad \\ \text{Cl} \quad \text{H} \end{array}$			$\begin{array}{c} \text{H}-\text{C}=\text{C}-\text{H} \end{array}$	
b.p. (°C), 760 mmHg): (-33.10 (g))	37 (32)	(11.31)	-84.0	54.19 (g)	(65.20)
ΔH_f : (-33.10 (g))	0.30 (g)	(-6.62)	0 (g)	53.89	(47.27)
(-33.10 (g))	-6.0 (l)	(5.01)		54.19 (g)	(65.20)
(-33.10 (g))	-6.0 (l)	(-12.92)	0 (g)		(47.27)
(-42.7 (l))	0.30 (g)	(20.91)			(74.80)
(-42.7 (l))	0.30 (g)	(2.98)			(56.87)
(-42.7 (l))	-6.0 (l)	(14.61)			(75.80)
(-42.7 (l))	-6.0 (l)	(-3.32)			(56.87)
$\begin{array}{c} \text{Cl} \quad \text{H} \\ \quad \\ \text{Cl}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{Cl} \quad \text{H} \end{array} \xrightarrow{-\text{Cl}_2} \begin{array}{c} \text{Cl} \quad \text{H} \\ \quad \\ \text{Cl}-\text{C}=\text{C}-\text{H} \\ \quad \\ \text{Cl} \quad \text{H} \end{array}$					
b.p. (°C), 760 mmHg): (-33.10 (g))	vinyl chloride chloroethylene				
ΔH_f : (-42.7 (l))	$\begin{array}{c} \text{Cl} \quad \text{H} \\ \quad \\ \text{Cl}-\text{C}=\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{C}=\text{C}-\text{H} \end{array}$	(41.5)	-84.0	54.19 (g)	(65.2)
	0 (g)	(51.1)	-22.09 (g)	23.7	(56.3)
	8.4 (g)		-40.02 (g)	5.77	

Notes: see notes Table A-1.

TABLE A-4

Enthalpy of formation of vinyl chloride (VC) from 1,1,2-trichloroethane (1,1,2-TCA) at standard temperature and pressure from standard enthalpies of formation

[illegible]

The enthalpies for the reaction of 1,1,2-TCA to form 1,1-DCE, *trans*-1,2-DCE and *cis*-1,2-DCE are presented in Table A-4. Values for the conversion to acetylene are also exhibited.

The values illustrate that the formation of DCE (negative values for the enthalpy of reaction) is more likely to occur than is formation of VC (positive values for the enthalpy of reaction). However, certain factors explained in the main text may increase the likelihood of both reactions.

We note that the enthalpies of the reactions for the second stage conversion into ethylene or acetylene are always highly endothermic indicating that they probably do not proceed spontaneously.