Study of Vinyl Chloride Formation at Landfill Sites in California

Final Report

January 1987

Prepared for the
State of California
California Air Resources Board
under Contracts A4-154-32
and 2311206978

Battelle
Pacific Northwest Laboratories

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"STUDY OF VINYL CHLORIDE FORMATION AT LANDFILL SITES IN CALIFORNIA"

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January 1987

ABSTRACT

Low concentrations of vinyl chloride (VC) gas have been detected in the air above California landfills, even where no material containing it has reportedly ever been dumped. The purpose of this study was to determine if vinyl chloride is produced _in situ_ by natural processes. Review of previous work indicated that biological action on other chlorinated ethylenes present in the landfills was the most likely source of vinyl chloride. Other emission sources are possible, ranging from illegal dumping and leaching to thermal decomposition of plastics. (An evaluation of illegal dumping was beyond the scope of this study.) Experiments were performed with landfill material obtained at depths of 3-16 ft from a Northern and a Southern California landfill, and with control material presumably never exposed to chlorinated compounds (Richland, WA, anaerobic digester sewage sludge). Test materials were incubated with a range of chlorinated compounds and with ^{13}C labeled trichloroethylene (TCE) to confirm biological production of VC from other compounds, including TCE. Pyrolysis experiments with PVC showed release of residual monomer but no VC formation. No VC was formed from TCE by photolysis or from heat- and radiation-sterilized landfill materials. VC formation was highest in experiments using the landfill material already containing the greatest amounts of organic compounds (and the most adapted microorganisms), and least with the "uncontaminated" sewage sludge. These experiments confirmed biological production as the most probable formation route for landfill emissions of VC and not chemical or photochemical routes of formation. Leaching from old PVC could be a minor source of VC, although there was less than 0.1% (estimated) plastic in the landfill samples containing at most, 330 ppm of VC monomer. A landfill sample known to produce vinyl chloride was used as a source of microorganisms for initiation of an anaerobic chemostat. Methanol was the only carbon supplied and carbon dioxide and methane were the main products indicating the presence of methanogenic bacteria. The enriched culture was homogeneous when grown on agar based medium under strictly anaerobic conditions in roll-tubes using methanol as the sole carbon source. Under aerobic conditions no colony growth of any kind was observed. When a sample of the enriched culture was incubated with

^{13}C-labeled TCE in the presence of methanol ^{13}C-labeled vinyl chloride was detected.

These experiments clearly show that microbial action on chlorinated solvents in landfills is the most probable source of observed VC formation *in situ*. Methods for minimizing future VC emissions from landfills are discussed.

ACKNOWLEDGEMENTS

The work of Emcon Associates, San Jose, CA, in obtaining landfill samples under subcontract #B-K8103-C-H to Battelle-Northwest, is gratefully acknowledged. This report was submitted in fulfillment of Contract # A4-154-32, "Study of Vinyl Chloride Formation", by Battelle, Pacific Northwest Laboratories under the sponsorship of the California Air Resources Board. Work was completed as of January 16, 1987.

DISCLAIMER

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SUMMARY AND CONCLUSIONS

This study was performed to determine whether observed emissions of vinyl chloride from municipal landfills in California are the result of *in situ* production by natural processes. Vinyl chloride is a gas that until about ten years ago was widely considered to be harmless and was subsequently identified as a potent carcinogen which gives rise to a rare form of cancer known as hemangiosarcoma. Exposure in ambient air in California is currently restricted to a 24-hour average of no more than 10 ppb. Emissions of vinyl chloride into air and groundwater in some cases have been found to exceed this limit, even where no material containing vinyl chloride was ever reportedly dumped. The sources of these emissions has been of increasing concern throughout the U.S.

Initial work was directed at generation of a list of potential vinyl chloride sources, and modes of formation based on published information. This initial list includes a wide variety of possibilities, some of which could be eliminated on the basis of available evidence, and others which required further experimentation and research. Possible sources initially considered included:

- Legal and illegal dumping of PVC production sludges
- Leaching of residual vinyl chloride from plastics
- Decomposition of PVC (polyvinyl chloride)
- Dechlorination of chlorinated solvents
- *In situ* synthesis from acetylene and chloride

An experimental approach was designed to test these various possible mechanisms and identify those which are actually occurring. To make the laboratory study more relevant to actuality, material samples were obtained from two California landfills (one Northern and one Southern). This material was used in most of the experiments, and was obtained from the surface and at two different depths below the landfill covers. A further source of raw material used in some experiments was a "clean" (solvent-free) sludge obtained from the City of Richland, WA, sewage treatment plant. The landfill conditions at the sampling points were recorded and used to define experimental conditions.

Detection and quantitation of vinyl chloride and other compounds was by means of a modified purge-trap technique based on EPA method 601. The major modification consisted of using a volatile compound chromatography column, with the first 1/3 of its length packed with Chromosorb 101 and the remaining 2/3 packed with Chromosorb 102. This modification permitted separation of water and more volatile compounds from vinyl chloride and gave complete separation of cis and trans-1,2-dichloroethylene (which is not achieved by the packed column used in the EPA 601 method).

Landfill samples were analyzed for both inorganic and organic components, and especially vinyl chloride and other chlorinated solvents. The Southern California site (designated Site A) contained more organic contaminants than the Northern site (designated B), in agreement with the sites' histories of dumping. Vinyl chloride was present in the gas taken after core drilling at Site A at a level of 5-7 ppm, but was not detected in the gas taken after core drilling at Site B.

Production of vinyl chloride from PVC plastics was measured directly by heating samples and monitoring the emitted gases by gas chromatography/mass spectrometry (GC/MS). PVC older than 10 years contained 330 ppm of residual monomer while a 1-year old sample contained only 3 ppm, reflecting industry attempts to reduce monomer levels. Pyrolysis to 650°C did not produce additional vinyl chloride monomer, in accordance with published data which indicates that PVC decomposes thermally by a dehydrochlorination mechanism. This results in formation of a linear polyene which cyclizes to the major observed pyrolysis product, benzene.

Further experiments were performed using 13-C-labeled trichloroethylene (TCE) as a marker compound. TCE is the most widely used solvent likely to be found in landfills and has been implicated as a vinyl chloride precursor. ^{13}C-TCE was used since it is non-radioactive and can easily be tracked by

GC/MS. Formation of ^{13}C vinyl chloride and dichloroethylenes provided conclusive proof of their origin from ^{13}C-TCE.

Photolysis of TCE to vinyl chloride at landfill surfaces exposed to sunlight was eliminated as a possible formation mechanism, by experiments in which labeled TCE was irradiated by UV light over landfill surface soil. In air, chloroacetylene was formed, while in argon no organic products containing labeled carbon were found. This is in accordance with literature reports indicating conversion of TCE to chloroacetaldehyde. Vinyl chloride itself is reported to have only a 4.5 hr half-life in sunlight in air.

Labeled TCE and a range of unlabeled chlorinated ethylenes and ethanes were incubated with landfill and sewage materials under simulated landfill conditions. Vinyl chloride was first detected after a 1-6 week lag period. When the experimental systems ("microcosms") were initially sterilized by autoclaving or by gamma irradiation, no vinyl chloride was produced. However, dichloroethylenes were produced from 1,1,2-trichloroethane under sterile conditions, indicating a biogenic formation route for vinyl chloride but that the chemical conversion of chloroethanes to chloroethylenes also occurs.

Landfill material was inoculated into an anaerobic fermentor and grown on methanol as a carbon source. Inoculation onto agar roll-tubes under anaerobic conditions resulted in growth of an apparently homogeneous species. The organism is a methanogen but an exact species identification has not been made. Conversion of ^{13}C-TCE to ^{13}C-VC by this organism has been confirmed.

These experiments led to the following overall conclusions:

- The most probable route for vinyl chloride formation in landfills is by the action of anaerobic bacteria on solvents such as TCE. Even in carefully controlled municipal landfills, some TCE would be present from paint products, duplicating fluids, and household materials.

- A secondary background level source of minor importance may be residual ("old") PVC plastics which can gradually be leached by water, especially at the relatively elevated temperatures of active landfills, and release their load of vinyl chloride.

- Other mechanisms (pyrolysis, surface photolysis, hydrolysis of TCE and related solvents) do not appear to be significant contributors to overall vinyl chloride formation.

- Interconversion of chloroethylenes and chloroethanes in landfills is a complex network rather than a simple forward pathway. Chloroethanes may be hydrolysed to chloroethylenes by abiogenic means. Vinyl chloride itself may be back-converted to 1,1-dichloroethylene.

- Within the limitations of this study (small sample size, limited numbers of samples, etc.), vinyl chloride appeared to be produced only where chlorinated solvents were present in the landfill.

RECOMMENDATIONS

The most probable primary source of vinyl chloride emissions from landfills is from the bio-degradation of trichloroethylene and related solvents, as determined during the course of this study. Monitoring of vinyl chloride emissions from landfills throughout the State of California is ongoing. Results to date support the hypothesis that vinyl chloride formation at landfill sites is dependent upon the presence of chlorinated solvents previously dumped. As can be seen from the solvent use profiles in Appendix A, the major use for chlorinated solvents is in degreasing of metal parts, followed by use as chemical intermediates and components in adhesives, aerosols, etc. Household use accounts for only 5% of the total use of, for example, trichloroethylene. By contrast, 85% of vinyl chloride production goes directly into PVC manufacture, and virtually all of the remainder is exported. Vinyl chloride users are well aware of the hazards associated with the use of the monomer gas and currently release only very small quantities into the environment. This was not the case ten years ago, however, when vinyl chloride was generally considered to be harmless in small concentrations, and large amounts of PVC production sludges containing residual monomer were dumped. Because of these considerations, and the fact that biodegradation of chlorinated solvents is slow, emissions of vinyl chloride may continue for many years after solvent dumping. The problem is therefore a long-term one, and will not disappear overnight even if dumping of chlorinated solvents is banned immediately.

Remedial measures which can be recommended include a range from merely palliative, to final solutions. We found no evidence for the de novo synthesis of vinyl chloride from simpler constituents; traces may occur this way, but the major source is from added solvents.

Currently, landfill gas emitted from hazardous dumps is collected and burned. This is an effective way of destroying vinyl chloride, and should be extended wherever practicable to non-hazardous waste landfills where vinyl chloride above a certain level (e.g., 10 ppb) has been detected.

The landfilling of all two-carbon based chlorinated solvents (ethylenes and ethanes) should be terminated forthwith. Preferably, all waste solvents of this type should be destroyed or recycled before leaving their site of use. Technical methods exist for doing this. Oxidation by incineration or electrochemical methods or pressurized high temperature aqueous alkaline destruction under development at Battelle-Northwest and elsewhere are quite effective.

Alternatives to the use of chlorinated solvents in household products which eventually find their way into municipal landfills should be sought. These only account for 5% of solvents dumped, but can provide a background of vinyl chloride in air and groundwater.

Research should be performed to investigate long-term, low cost methods for vinyl chloride trapping or destruction. One example would be to apply the technique of *in situ* bioconversion by developing aerobic bacterial strains which can degrade vinyl chloride, and seeding them onto landfill covers.

Fortunately, the half-life of vinyl chloride in air and sunlight is quite short, and for this reason widespread health-threatening concentrations are unlikely to occur. (The State of California Ambient Air Quality Standard for Vinyl Chloride is 10 ppb, the lowest level that can at present be reliably detected.)

Perhaps the most feasible control method is the collection and burning of landfill gases. Topsealing prevents random dispersal of the gases, but does however cause formation of positive gas pressure. This pressure is often relieved by lateral gas movement which can cause problems in neighboring buildings. Gas pressure must therefore be relieved. Treatment of the gases to remove toxic and odoriferous components is then necessary, and combustion may be the most economical method. Care needs to be exercised in order to maintain combustion conditions where complete oxidation of all toxic components occurs. A longer term approach may be to minimize the amounts of chlorocarbons deposited in landfill operations in the future.

INTRODUCTION

PROJECT SCOPE AND PURPOSE

This study was designed to identify the sources of observed emissions of vinyl chloride in the air over California landfills, both industrial and municipal. At the time the study was begun, various modes of origin of the vinyl chloride being considered included possible illegal dumping of PVC sludges, PVC thermal destruction *in situ*, biological conversion of chlorinated solvents, and chemical reactions. As a first step in developing suitable control and/or remediation approaches it was necessary to pinpoint the actual sources of the emissions by critically examining reports of research already performed.

Vinyl chloride is a bulk industrial chemical. Almost 7 billion pounds were produced in the U.S. in 1985 in 11 plants in Louisiana, Texas, and Kentucky. It was used almost entirely in the production of PVC (polyvinyl chloride). Until about 10 years ago it was considered to be a virtually non-toxic anaesthetic gas. It was subsequently identified as a potent carcinogen responsible for a rare type of hemangiosarcoma. Restrictions on exposure were promptly applied, and at present the maximum 24-hour average ambient air exposure limit in California is 10 ppb. Concurrently with a gradual reduction in exposure limits to vinyl chloride, monitoring of trace organic emissions in air from landfills in California was widened to include chlorinated hydrocarbons. In some cases, vinyl chloride was identified as a component of these emissions, at concentrations above the 10 ppb exposure limit. It therefore became a matter of concern to identify the sources(s) of these emissions so that steps could be taken to control them. Emissions of vinyl chloride from landfills in California was particularly surprising in view of the fact that no vinyl chloride is currently produced in that state.

A review of existing literature information was undertaken as a first step in meeting the project objectives. This allowed some probable routes for vinyl chloride formation to be identified, and also permitted tentative elimination of some theoretically possible routes based on negative experimental evidence. Following this an experimental plan was developed with the intent of confirming the formation of vinyl chloride by the most probable routes, and eliminating other possible routes. This plan was based as far as possible on an examination and use of actual landfill material so that the results would be directly applicable to the real-life situation in California.

This study was undertaken to meet the above objectives by the quickest research route and to provide information which can be used to help in solving an environmental problem. It was limited in the number of landfill samples we could obtain and the amount of analytical work which could be performed in working with them. We make no claim that the landfill material samples are "representative", although we hope they were typical. Similarly, purge-trap analyses for vinyl chloride are accurate, but at the expense of total recovery of higher molecular weight solvents from the vial samples. We have not performed detailed reaction kinetic determinations on TCE and other solvent biodegradation as this was outside the project scope, but rather have identified the major routes for vinyl chloride formation.

SURVEY OF PRIOR WORK

The purpose of this introductory survey is to summarize available information on various potential mechanisms for vinyl chloride formation and emission from waste dumps, and to generate a list of mechanisms in order of their likely contribution to the overall emission. Key references or reviews are used to illustrate available evidence for or against a particular mechanism rather than a complete review of all available documents.

The reason for concern about vinyl chloride emissions lies in recent evidence that the gas, long considered harmless, is in fact a potent carcinogen and mutagen. For example, the entry for vinyl chloride in the Kirk-Othmer encyclopedia (Brighton, 1974) quotes Industrial Hygiene (1963): "A detailed study using rats has shown that repeated daily exposure to concentrations of 2-5% of vinyl chloride causes no permanent damage. It has been confirmed from 5 minute exposures of human subjects to vinyl chloride in concentrations of up to 2.0% that a concentration of about 600 ppm is required to produce minimum effects of anesthesia under continuous exposure". The physical properties of vinyl chloride are summarized in Table 1. By comparison, Hefner et.al. (1975) state that: "Vinyl chloride monomer.... has been associated with the development of angiosarcoma and portal cirrhosis of the liver as well as other untoward effects in workers exposed to unknown but undoubtedly high concentrations of VCM." Other more recent research resulted in the continued downward movement of vinyl chloride maximum permissible exposure limits, beginning at 10 ppm (EPA, Fed. Reg., 1976; Lamorte, 1978; Dimmick, 1981).

The existence of vinyl chloride emissions from landfills has been known for some years, as has the presence of vinyl chloride in leachate water (vinyl chloride is slightly soluble in pure water). The major question to be answered in this study is the root cause of the vinyl chloride presence: Is it a result of past dumping of materials containing vinyl chloride, or is it being generated in situ, and if so, from which precursors? The potential approaches to identifying key experiments to decide this issue are many. We chose an approach which combines observational evidence with logical deduction. The conclusions reached in this brief review of existing evidence were used to produce an experimental plan to further define the exact mechanism for vinyl chloride emissions. Hopefully, further work (beyond the scope of this project) will then be done to identify ways of preventing or suppressing such emissions in the future.

Much of the basic work performed to date has consisted in monitoring vinyl chloride and other chemicals in air and water in the region of production facilities and toxic chemical dumps. Information to 1980 on atmospheric trace organic contaminants over the continental U.S. has been compiled in one document listing 151 chemicals (Brodzinsky and Singh, 1983). A study of volatile organic compound concentrations in the air of the New Jersey/New York area has also been published (Kebbekus and Bozzelli, 1983), and lists data for 27 different compounds, including vinyl chloride and several other halogenated hydrocarbons. A number of states have developed programs for ambient air monitoring and analysis of trace organic contaminants. The State of California approach and some results are presented in two recent papers by Venturini et.al. (1985) and Kowalski et.al. (1985).

Table 1: Physical Properties of Vinyl Chloride Monomer

Property	Numerical Value	Property	Numerical Value
M. Wt.	62.501	Critical Temp.	158.4
B. Pt.	-13.37	Critical Press.	52.2 atm.
F. Pt.	-153.79	Dielect. const.	6.26
Flash Pt.	-78		
Refractive index	1.398	Liquid density	
Sp.Ht. liquid	0.38	-20	0.98343
Latent Ht. vap'n	71.26	-25	0.99176
Latent Ht. fusion	18.14	-30	0.99986
Ht. formation (cal/g.-mole)	9000	Viscosity, cp	
		-10	0.248
Vapor Press., mm		-20	0.274
25	3000	-30	0.303
-13.37	760	-40	0.340
-55.8	100		
-73.9	30	Surf. tens.,dyne-cm	
-87.5	10	-10	20.88
-109.4	1	-20	22.27
		-30	23.87

All data in ^{o}C, grams, cal. unless otherwise stated. Dielectric constant at 105 Hz and 17.2^{o}C. After Brighton (1974).

Volatile organic compound emissions from municipal waste landfills have become a cause for concern in a number of states because of the potential hazard to local inhabitants from landfill gases. One example was described by Walsh (1984) for the Lees Lane (OH) and Port Washington (NY) landfills. Both are municipal landfills, and in the Port Washington facility particularly, no hazardous wastes were permitted and the restriction was reportedly stringently enforced. However, analysis of the landfill gases showed the presence of dichloroethane among other components at the Lees Lane site. (The isomer was not identified.) 1,2-Di-chloroethane is used mainly in the manufacture of vinyl chloride, but does have significant domestic uses. Until 1982, Stauffer Chemical produced 1,2-dichloroethane in the Los Angeles area. It was used in pesticides, solvents, gasoline, and in solid fuels as well as for vinyl chloride manufacture. The efficiency of screening of materials dumped at the sites may therefore be open to question. Other halogenated materials identified could conceivably come from paints, solvents, etc. from non-industrial manufacturing uses. Vinyl chloride and other compound concentrations in monitoring well gases at these sites were determined over a 2 year period. At Lees Lane the mean vinyl chloride concentration was 28 ppm (range 0-188 ppm) and at Port Washington it was 15.84 ppm (no range reported). Controls applied to these landfills consisted of extraction and blower systems to divert the effluent gases to atmosphere away from homes and schools in the areas concerned. Gas incineration is being considered. This example illustrates the magnitude of the problem and the lack of efficient methods of dealing with it. Data on the concentrations of chlorocarbons measured in monitoring wells located in these landfills is presented in Tables 2 and 3.

Data such as that presented in Tables 2 and 3 is indicative of the problem, but should not be considered as representing the situation in California landfills in any quantitative manner. Differences in sampling techniques, materials, and data interpretation can lead to quite different results from one landfill to another, regardless of variations in chemical composition. On-site monitoring by portable gas chromatographs can in principle eliminate many of the errors in sample collection, transportation, and handling.

In the example given by Jacot (1983), a "typical" (unidentified) landfill was described: It had been in use since the late 1930's, with waste being burned at the site until the early 1960's. Landfilling began in the mid-1960's and incineration was discontinued, and only municipal waste has been accepted since the mid-1960's. Vinyl chloride was detected (16 ppm) at one of the monitoring points near the center of the landfill, and is presumably being formed from solvents dumped years ago. However, the fact that vinyl chloride is also being emitted from municipal dumps supposedly free of hazardous material is significant, as is the fact that there are measurable amounts of dichloroethane, di-, tri- and tetrachloroethylenes present in association with the vinyl chloride. So far none of the literature examined has shown vinyl chloride production in the absence of detectable amounts of these other materials. (The term "-chloroethylenes" is used here rather than the alternative "-chloroethene" for consistency with other reports and common usage).

Table 2: Lees Lane Landfill Trace Gas Analysis (after Walsh, 1984).

Compound	Mean Concn.*	Range	# of Analyses	OSHA Level
Benzene	8	0-46	15	10
Butadiene	3	-3-	1	1000
Cyclohexane	2	0-19	15	300
Dichlorodifluoromethane	6	0-25	14	1000
Dichloroethane[+]	6	0-22	15	100
Dichloroethylene[+]	40	-40-	1	200
Ethylbenzene	6	0-27	15	100
Heptane[+]	2	0-15	7	400
Hexane[+]	6	0-37	16	50
Toluene	15	1-175	15	200
Vinyl Chloride	28	0-188	44	1
Xylene	10	0-45	7	100

* All data in ppm.

[+] Compounds named as in original report; isomers not specified.

Table 3: Port Washington Landfill Trace Gas Analysis (after Walsh, 1984).

Compound	On-Site*	Homes	School	OSHA Limit[+]	NYS Limit
Benzene	--	5.1	3.0	10,000	33
Toluene	2,930	9.5	2.5	200,000	2000
Xylene	--	-	-	100,000	333
1,1,1-Trichloroethane	200	1.1	-0-	350,000	7000
1,1,2-Trichloroethane	--	-	-	10,000	33
Tetrachloroethylene	300	1.4	-0-	100,000	167
Trichloroethylene	80	-	-	100,000	333
Vinyl Chloride	15,840	-0-	-0-	1,000	0.16

* Wells

[+] All values in ppb.

Attempts are being made to establish standard techniques and methods for waste site analysis and monitoring (Ford and Turina, 1985; Ford et.al., 1985; Plumb, Jr., 1984; Pellizzari et.al., 1984), so that data from one site can be applied to another, but it is a difficult problem.

Information on vinyl chloride in leachate water from waste dumps can also be used to infer mechanisms for vinyl chloride formation, although in this case the relatively high solubility of vinyl chloride in water compared with the higher molecular weight chlorocarbons can "skew" quantitative results. An additional cause for confusion is the frequent error in the identification of cis-dichloroethylene as the trans- isomer, due to the inability of the standard EPA 601 analytical method (using a packed GC column) to separate the two (Cline and Viste, 1984). Three studies on groundwater contamination by vinyl chloride are indicative of the current state of research:

Pennington (1983) performed a hydrogeological investigation at the abandoned Price Landfill hazardous waste site (Pleasantville, NJ, west of Atlantic City). This investigation was instigated as a result of a lawsuit by citizens concerned about drinking water contamination, and consequently had to be performed quickly. Vinyl chloride was detected in the water leachate plume together with other chlorocarbons, and was also present (up to 33 ppb) in some surface water. Up to 650 ppb of vinyl chloride was present in drainage areas down gradient from an equipment storage site, and 380 ppb was found emanating from an illegal dump site. Table 4 lists the compounds and their concentrations identified in the latter samples. Highest concentrations of vinyl chloride were again associated with high concentrations of other chlorinated materials.

Sabel and Clark (1983) reported a compilation of data on organic compound contamination of leachate water from 6 Minnesota municipal solid waste landfills, as well as 5 from Wisconsin and one from New York. Their conclusions were that dichloromethane (methylene chloride), trichloroethylene, 1,1-dichloroethane (not 1,2-), and trans-1,1-dichloroethylene were ubiquitous. (There are no cis-/trans- isomers of 1,1-dichloroethylene, which error also casts doubt on the identification of 1,1-dichloroethane rather than the normally encountered 1,2- isomer). Vinyl chloride was detected in water from 3/13 of the sites sampled and from one of the 4 Wisconsin sites (at 61 ppb).

Table 4: Water-Borne Contaminant Concentrations at Price Landfill Illegal Dump Site (Pleasantville, NJ) (after Pennington, 1983).

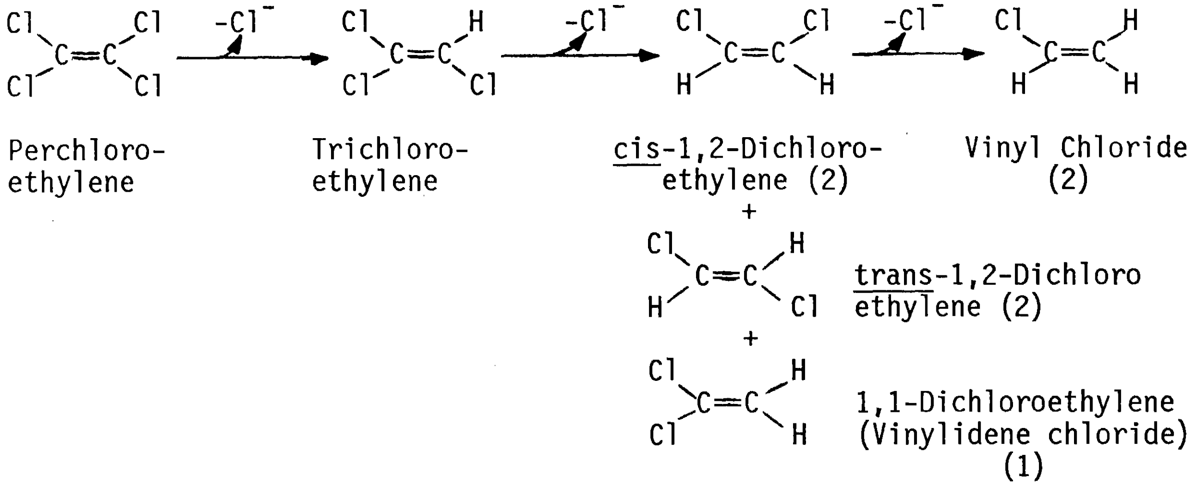
Compound	Depth (in.)			
	0-9	15-27	43-47	56-62
Benzene	**	190*	100	<75
Chloroform	**	<100	<75	<75
1,2-Dichloroethane	**	570	<75	<75
Trans-1,2-dichloroethylene	**	<100	<75	<75
Dichloromethane	**	765	250	<75
Toluene	**	**	230	100
Trichloroethylene	**	150	<75	130
Vinyl Chloride	**	*380*	<75	<75
Petroleum Hydrocarbons (%)	32	0.5	0.9	1.1

* All values in ppb except for petroleum hydrocarbons (%).
** Target compound masked by large amounts of other VOC's.

The third study is the most interesting, because it attempts to correlate migration and degradation patterns of the volatile organic compounds observed in waste site water leachates. This study (Cline and Viste, 1984) identifies the dechlorination pathway for formation of vinyl chloride from polychlorinated solvents (following page).

The data presented includes municipal solid waste landfills, industrial chlorinated solvent recovery facilities, and an industrial site. The concentrations of primary compounds and breakdown products were generally correlated with distance from the landfill site, amounts of primary materials dumped, the presence of biodegradable material to support anaerobic digestion, depth, and flow direction. This evidence strongly supports the hypothesis that vinyl chloride is formed as a result of reductive dechlorination of common chlorinated solvents by anaerobic bacteria. However, before this conclusion is confirmed, it is necessary to consider *all* reasonable formation mechanisms to provide a basis for comparison. The evidence for vinyl chloride formation by biological and other mechanisms is summarized in the following pages.

Chloroethylenes


Perchloroethylene

Trichloroethylene

cis-1,2-Dichloroethylene (2)

Vinyl Chloride (2)

trans-1,2-Dichloroethylene (2)

1,1-Dichloroethylene (Vinylidene chloride) (1)

Chloroethanes

$$Cl_3C{-}CH_3 \xrightarrow{-Cl^-} Cl_2CH{-}CH_3 \xrightarrow{-Cl^-} ClCH_2{-}CH_3$$

1,1,1-Trichloroethane (2) 1,1-Dichloroethane (1) Chloroethane (1)

(1) Substantial degradation; (2) slow degradation

Vinyl Chloride Formation Routes:

The various means by which vinyl chloride may be formed in landfills (both toxic chemical waste and municipal dumps) can be classed as leaching, chemical, photochemical, and biological. Each is briefly defined below:

Leaching

Vinyl chloride emission may result from the physical transportation to the surface of vinyl chloride monomer already present in the landfill. Although vinyl chloride is a gas under normal conditions (b.p. -13°C), it is present in solution or entrapped as the monomer in waste sludges from PVC manufacture, and in pre-1975 fabricated materials such as PVC pipe and film (e.g., Saran wrap). Recent legislation has considerably reduced the permissible levels of vinyl chloride monomer present in these materials, but significant amounts of older material are still present in landfills and could be contributing to the emission problem.

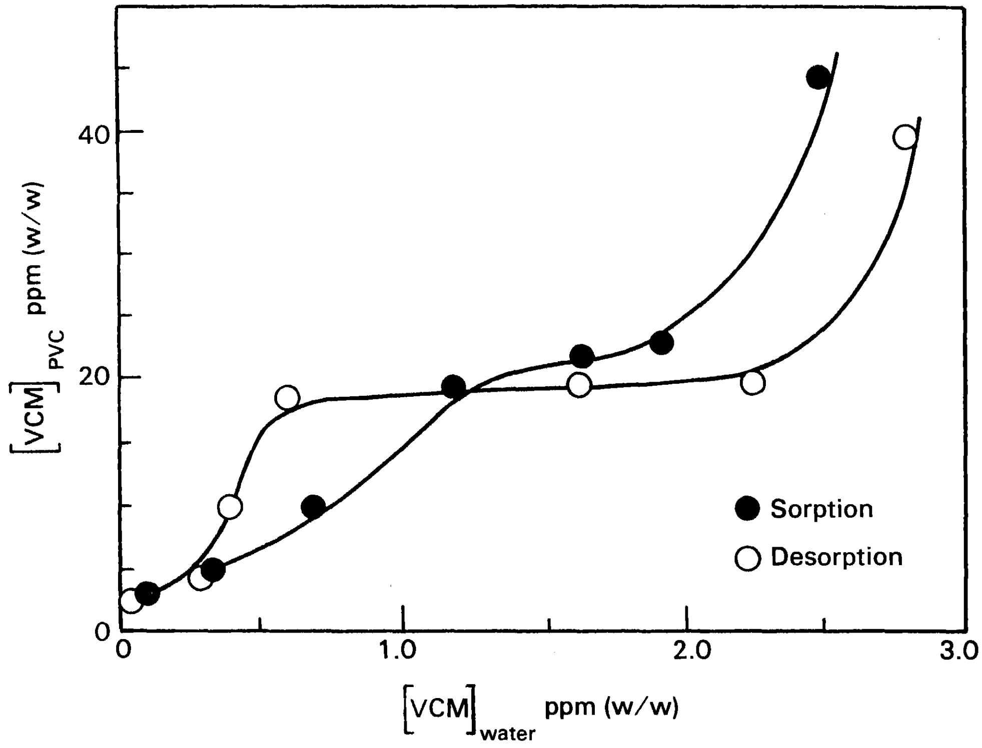
The problem of vinyl chloride monomer emission from waste PVC sludges has been addressed by Markle et.al. (1976), who took waste PVC sludges from a number of industrial sources and analyzed them for monomer content. The concentrations of monomer found ranged from 7 to 520 ppm in the wet filtered sludges (20 - 1260 ppm dry solids basis). These sludges were reportedly dumped in industrial and in municipal sites and could therefore be a contributor to observed vinyl chloride emissions from some municipal sites. Release rate studies performed using these sludges under simulated landfill conditions showed a rapid initial release rate, followed by a slower release of the major amount of vinyl chloride over a much longer time. A background air concentration of 100 - 300 ppb of vinyl chloride was observed at landfills where PVC sludges have been disposed of for several years, although up to 1000 ppb could be detected 1.5 m above the ground for up to 24 hr after the sludges were covered. Although this amount of vinyl chloride is significant, and may account for part of the observed emissions, it does not account for all of the observed 50 ppm of vinyl chloride in air noted above some industrial waste landfill sites in California, some 10 years after PVC sludge dumping was prohibited.

The equilibrium distribution of vinyl chloride monomer between PVC powder (0.15 - 0.25 um) and water has been determined (Kontominas et.al., 1982) (Figure 1), and is definitely non-linear with concentration in the polymer. At 22°C, and above 20 ppm, the desorption curve becomes almost exponential in nature. In PVC sludges, with high initial vinyl chloride content and small particle size, a very rapid desorption into the aqueous phase would occur. Exchange with gas evolved from anaerobic digestion of cellulosic materials in the landfills would then transfer the monomer to the air. This study supports the conclusions already noted, that vinyl chloride emissions from film and sludges is a contributor rather than the main cause of observed emissions.

Chemical

Chemical formation of vinyl chloride is considered to involve mainly the degradation of PVC (polyvinyl chloride) and chlorocarbons through the action of heat, alkali, or metal ions. An alternative route, in situ synthesis from

Figure 1. Sorption and Desorption Isotherms for PVC-VC-Water at $22^{o}C$.



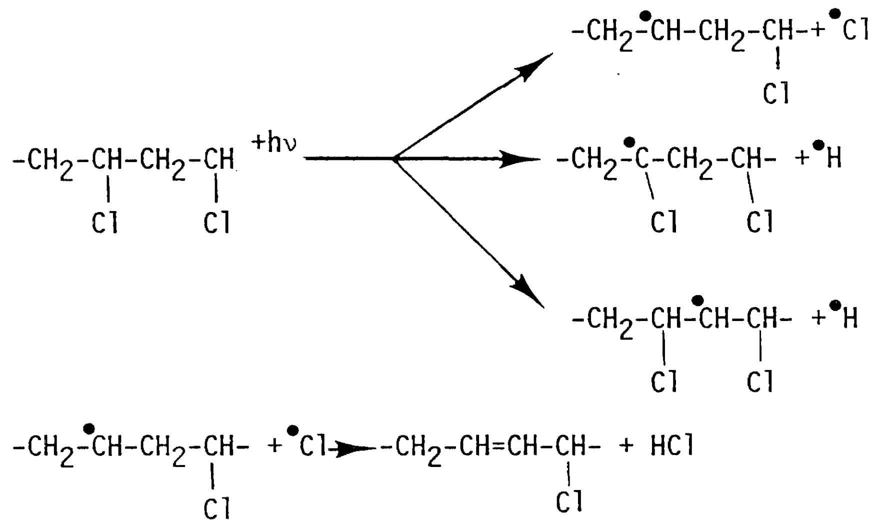
(After Kontominas et.al.(1982).

acetylene and hydrogen chloride in the presence of mercuric ion catalysts (based on the now obsolete process for vinyl chloride manufacture) is unlikely to occur in landfills, based on our present understanding of landfill conditions. Careful review of the available literature indicated that the chemical degradation route contribution to vinyl chloride emissions is at best, minor. Consideration of the various degradation routes which have been established for these substances shows the reasons for this.

(a) Polyvinyl chloride:

The processes involved in thermal, photolytic, and high-energy degradation of PVC have been reviewed up to 1975 by Close and Gilbert (1977). PVC degradation (either thermal or photolytic) involves loss of hydrogen chloride and formation of an unsaturated group. This general mechanism is illustrated in Figure 2:

Figure 2. Mechanism of PVC Degradation. (After Close and Gilbert (1977).



Further loss of hydrogen chloride from adjacent sites, catalyzed by the HCl already lost, results in formation of a polyene. After approximately 6 conjugated double bonds are formed, chain stability has decreased to the point where scission occurs. In the presence of air, this is facilitated by oxidation. In the absence of air, ring formation and evolution of benzene occurs. Other aromatic hydrocarbons and chlorobenzenes are minor products. The overall composition of these minor products varies with the PVC composition (additives, plasticizers, pigments, etc.). Levels of vinyl chloride occurring as products of side reactions have been reported as contributing no more than 0.25-0.7 mg/g of PVC between 200-600°C. (Boettner et. al., 1969). Lewis (1975) was able to detect no vinyl chloride monomer from pyrolysis at 225°C. A maximum of 35 ppm was found at 350°C for PVC degraded in air, and a maximum of 6 ppm was found at 500°C after thermal degradation in helium.

The only places within landfills where these temperatures would exist is in regions where degradation of waste organic material has resulted in spontaneous combustion. Under such situations, up to 35 ppm of vinyl chloride monomer could be formed from waste PVC. The PVC content of a typical landfill is not very great (we estimate a maximum of 0.1% by weight), and combustion would be noted by smoke, carbon monoxide, benzene, and other emissions. Vinyl chloride monomer emission has not been associated with combustion in any of the literature reviewed. Since such an association would almost certainly have been noted, we conclude that thermal degradation of PVC is not a significant cause of the observed vinyl chloride formation.

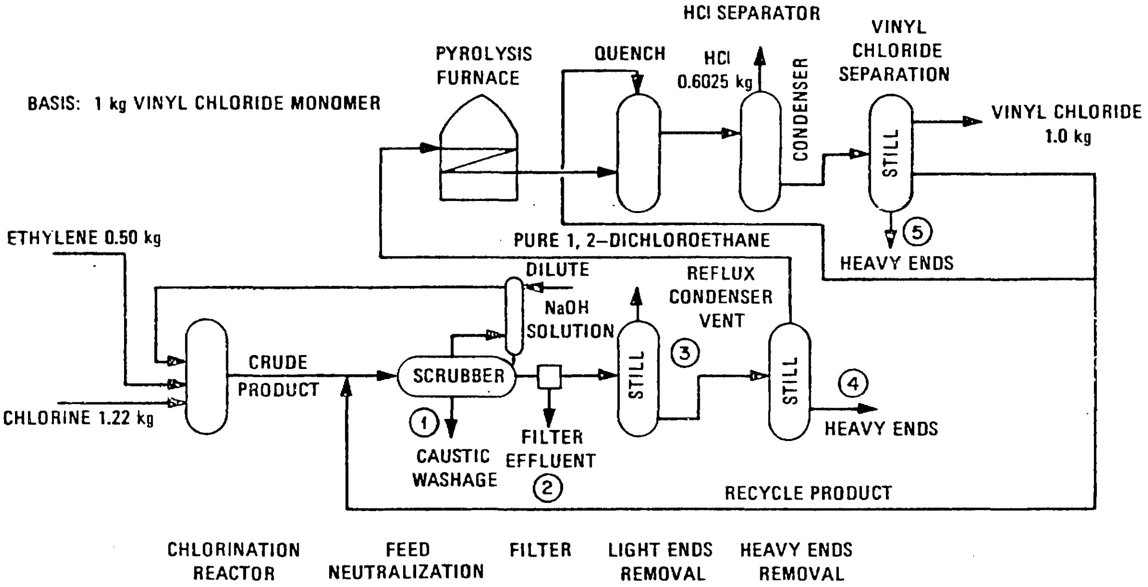
(b) Chlorocarbons.

1,2-Dichloroethane prepared from chlorination of ethylene is the major industrial precursor for vinyl chloride, from which it is produced by pyrolysis at 400°C or higher. In 1974 over 86% of the dichloroethane produced in the U.S. was used for vinyl chloride monomer production (Drury and Hammons, 1979). Figure 3 shows the distribution of pollutants, including dichloroethane, resulting from vinyl chloride monomer production from dichloroethane pyrolysis.

Dumping of chlorinated solvents could conceivably lead to vinyl chloride formation if pH and temperature conditions were right. In the absence of spontaneous combustion conditions, the maximum temperature likely to be achieved in any landfill is that of the maximum for anaerobic digestion. Composting (a technique used for digestion of sewage sludge and for killing of all pathogens) normally generates up to 55°C at maximum, and this is held for only a few days after addition. As soon as the cellulosic portion of the waste is digested, the temperature drops back towards ambient. However, under landfill conditions, with a heavily insulating overlay of soil, much higher temperatures can be generated and held for greater periods (years in some cases). Under certain conditions (i.e., addition of chlorinated solvents and alkali together) there could be some vinyl chloride formation. The rate is likely to be very slow. There is also competition with direct hydrolysis, which is favored in an aqueous environment. On the other hand, the persistence of 1,2-dichloroethane is high. Radding _et. al._ (1977) calculated a half-life for 1,2-dichloroethane at pH 7 and at 25°C of 50,000 years, based on a hydrolysis rate constant of approximately 5 x 10(exp-13) sec(-1).

The presence or absence of alkali associated with dichloroethane in landfills may therefore have some influence on vinyl chloride emissions. Examination of the waste streams (Figure 3)(Drury and Hammons, 1979) from dichloroethane conversion to vinyl chloride reveals that alkali is in fact used and dumped to land together with some dichloroethane. Vinyl chloride

Figure 3. Waste Products From Vinyl Chloride Production Process. (Drury and Hammons, 1979).



① CAUSTIC WASHAGE (WATER)

DICHLOROETHANE	0.00435 kg
SODIUM HYDROXIDE	0.00098 kg
SODIUM CHLORIDE	0.00033 kg
VINYL CHLORIDE	0.00098 kg
METHYL CHLORIDE	0.00085 kg
ETHYL CHLORIDE	0.00085 kg

↓

TO WATER

② FILTER EFFLUENT (SOLID)

TARS	TRACE
SOLIDS (AS CARBONS)	0.00008 kg

FILTER EFFLUENT (LIQUID)

DICHLOROETHANE	0.0005 kg
SODIUM HYDROXIDE	TRACE

↓

TO LAND

③ VENT ON REFLUX CONDENSER (GAS)

ETHANE	0.0049 kg
DICHLOROETHANE	0.012 kg
METHANE	0.0049 kg

↓

TO AIR

④ HEAVY ENDS

DICHLOROETHANE	0.0024 kg
1, 1, 2–TRICHLOROETHANE	0.004 kg
TETRACHLOROETHANE	0.004 kg
TARS	TRACE

↓

TO LAND

⑤ HEAVY ENDS

HEAVY ENDS	0.037 kg
DICHLOROETHANE	0.0008 kg
TARS	0.00005 kg
SOLIDS ASH	0.0002 kg

↓

TO LAND

wastes are dumped to water - although more severe legal restrictions since 1979 will have reduced this considerably. The "heavy ends" waste stream would be the major problem in industrial landfills. Municipal landfills should not contain any of this material, however. (Also, measured pH at the collection sites for material used in our experimental work was never greater than 6.4.)

Information on other halogenated solvents is more difficult to assess. Trichloroethylene and perchloroethylene (tetrachloroethylene) are mainly used in dry cleaning, an industry which practices stringent recovery of solvents for economic and environmental health reasons. Charcoal filters used for vapor absorption are regenerable, and require replacement only every 15 years or so. The total solid waste production by the entire industry was estimated as 132 tons by 1995 (Goodwin and Hawkins, 1980). Furthermore, these solvents are even more resistant to hydrolysis than dichloroethane, because of the presence of the double bond, and would not be expected to yield vinyl chloride. Addition of water to the double bond in trichloroethylene followed by elimination of hydrogen chloride would yield dichloroethanal by rearrangement, while direct elimination of hydrogen chloride would produce dichloroacetylene. Further conversion of these molecules would not produce vinyl chloride.

Photochemical

One possibility for the formation of vinyl chloride that must be considered is that the vinyl chloride is formed by photochemical reactions occurring at the landfill surface, possibly catalyzed by the landfill cover material. For example, in principle the activation of 1,2-dichloroethane by sunlight could lead directly to vinyl chloride through elimination of hydrogen chloride, by analogy with the thermal process for vinyl chloride manufacture. Examination of the detailed literature on photochemical reactions of chlorinated hydrocarbons shows that this is most unlikely to happen to any significant extent in reality, provided that the photochemical degradation takes place in the presence of air. This is because the initially formed activated radical promptly reacts with oxygen, nitric oxide, hydroxyl radical, and other trace atmospheric components, leading to a degradation sequence which does not involve vinyl chloride.

Dilling et.al. (1976) investigated the solar photodecomposition rates of a number of chlorinated compounds in the presence of 10 ppm of nitric oxide. Their data is summarized in Table 5. The half-life of vinyl chloride was determined to be 4.3 hr under these conditions, which included a 2.6x solar UV intensity, compared to summer noon at Freeport, TX.

Table 5. Photodecomposition Rates of Chlorocarbons (after Dilling et.al. (1976).

Compound	Half-Life* (hr)	Compound	Half-Life (hr)
1,1-Dichloroethylene	2.1	Dichloromethane	<5%/24 hr.
Cis-1,2-Dichloroethylene	3.0	Tetrachloroethylene	14.2
1,1,1-Trichloroethane	<5%/23.5 hr.		
Trichloroethylene	3.5	Ethyl acetate	14.6
Vinyl Chloride	4.3	Toluene	6.8

* Time for 50% disappearance in simulated atmospheric conditions; 10 ppm each of compound and Nitric Oxide.

Solar-assisted catalytic decomposition of trichloroethylene and chloroform has also been reported, using a titanium dioxide catalyst in an aqueous environment (Ahmed and Ollis, 1984). The products were carbon dioxide and hydrogen chloride. This system offers promise as a method of cleaning contaminated water. A similar sort of catalysis could in principle occur at the surface of a landfill, between sunlight, chlorocarbon vapors, water, and the inorganic soil matrix. However, as already noted, the products do not include vinyl chloride. If the UV frequency is lower (i.e., below the atmospheric absorption cut-off), vinyl chloride is produced from the radiolysis of 1,2-dichloroethane by an α,β-elimination route:

$$\mathrm{CH_2ClCH_2Cl^{\dagger}} \xrightarrow{M} \mathrm{CH_2ClCH_2Cl^{\dagger\dagger}}$$

$$\rightarrow \mathrm{C_2H_4} + 2\mathrm{Cl}\ (\text{or}\ \mathrm{Cl_2^{*}} \rightarrow 2\mathrm{Cl})$$

$$\xrightarrow{\alpha,\beta} \mathrm{C_2H_3Cl} + \mathrm{HCl^{*}}\ (\mathrm{HCl^{*}} \rightarrow \mathrm{H} + \mathrm{Cl})$$

$$\rightarrow \mathrm{CH_2Cl\bar{C}H^{*}} + \mathrm{HCl^{**}}\ (\mathrm{HCl^{**}} \rightarrow \mathrm{H} + \mathrm{Cl})$$

$$\mathrm{CH_2Cl\bar{C}H^{*}} \rightarrow \mathrm{C_2H_2} + \mathrm{HCl}$$

(Yano and Tschulkow-Roux, 1980).

At least part of the vinyl chloride is formed through molecular reactions and is independent of the presence of radicals such as nitric oxide. Salomon et.al. (1979) attributed formation of vinyl chloride and 1,1,2-trichloroethane from 147 nm photolysis of 1,2-dichloroethane to disproportionation of intermediate dichloroethyl radicals by chlorine atom transfer. Similarly, vinyl chloride can be formed from chlorocarbons by the action of laser light, which generates very high energies in the receptor molecules. The sequence involved in hydrogen chloride elimination from 1,2-dichloroethane to form vinyl chloride has been investigated by Schneider (1981), who used a laser system. This study was done with the objective of replacing the present vinyl chloride production process with a laser-driven process instead of a thermal pyrolysis. Caballero and Wittig (1983), using pulsed CO_2 laser light (infrared), showed that the primary reaction of trichloroethylene was elimination of hydrogen chloride to form dichloroacetylene, which further decomposed with loss of chlorine atoms. Vinyl chloride was not produced. Reiser et.al., (1979), using a similar system, obtained similar results, and also showed that vinyl chloride was dissociated to hydrogen chloride and acetylene. Confirmation of this route was obtained by Moss et.al. (1981) using a UV light source at 193 nm, and determining products by infrared emission spectroscopy. Using mass spectrometry and molecular beam techniques, Sudbo et.al. (1978) did find vinyl chloride as a product from trichloroethylene. However, this sort of reaction condition may pertain during lightning storms, but is not a normal condition in landfills. Finally, the gamma- and neutron radiolysis of aqueous trichloroethylene has been investigated by Sasse (1967), and found to liberate sym-tetrachloroacetone and 1,1,2-trichloro-1-propene, as well as chloride, hydrogen peroxide, hydrogen, carbon monoxide and dioxide, and glyxoylic acid. The formation of oxygenated products from application of ionizing radiation to halocarbons appears to be a normal process in the presence of air and water.

No evidence has been found for in situ formation of vinyl chloride from acetylene and hydrogen chloride in the presence of a mercuric ion catalyst. Hydrogen chloride is formed from PVC degradation but would be expected to react rapidly with the landfill matrix to form inorganic salts. Acetylene production is not a normal event during anaerobic digestion, and acetylene emissions have not been noted from landfills. Finally, dumping of mercury salts is strictly controlled and has been for many years. The presence of significant amounts of mercury contamination in landfills would long ago have been noted.

Biological Routes:

By far the greatest amount of direct experimental evidence favors formation of vinyl chloride monomer from sequential reductive dechlorination of chloroethylenes by anaerobic bacteria. This evidence will now be summarized.

Research performed since 1980 has proven that vinyl chloride may be produced biologically from chlorinated ethylenes (e.g., Barrio-Lage *et.al*. (1986); Vogel and McCarty (1985); Parsons *et.al*., (1984). The potential for production of vinyl chloride from chloroeth*a*nes has been suggested by Cline and Viste (1984). Another conceivable route for microbial vinyl chloride production is the breakdown of chlorinated aromatic hydrocarbons. Microbial degradation of aromatic compounds proceeds *via* an oxidative ring cleavage which yields small fragments of the original rings which can retain chlorine atoms (Alexander, 1965). The chlorine atoms are eliminated in subsequent metabolic steps. Other biological reactions which could also yield vinyl chloride are β-elimination from a halogenated compound yielding a double-bonded chlorinated compound such as vinyl chloride, dehydration reactions, and β-cleavage of aliphatic compounds. No evidence has been found in the literature for vinyl chloride production by any of these mechanisms. Another potential mechanism, microbial attack on PVC, seems unlikely since PVC is known to be resistant to microbial degradation (Pantke, 1977).

The only documented mechanisms for biological vinyl chloride formation use two-carbon chlorocarbons as substrates. The other mechanisms briefly considered above do not really appear reasonable in the light of our current understanding of biologically catalyzed reactions. Thus, in the following discussion the only mechanisms that will be considered are those using chloroethylenes or chloroethanes as substrates.

1. Vinyl Chloride Formation from Chlorinated Ethylenes:

Several research groups have shown that chlorocarbons are dechlorinated by a reductive dechlorination mechanism. One of the earlier studies is that of Wood et.al. (1981), who reported the presence of apparent by-products from biological degradation in groundwater. Specifically, vinyl chloride, 1,1-dichloroethylene, and cis- and trans-1,2-dichloroethylene were observed where only tri- and tetrachloroethylene had been released to groundwater. These compounds were thought to represent biodegradation products. Laboratory investigations were conducted to confirm this. Samples were incubated in septum vials which had been seeded with bottom sediments along with samples of contaminated surface water from the same site. Anaerobic conditions developed in the vials because of the high total organic carbon concentration of the surface water (approximately 25-40 mg/l TOC), and limited amounts of oxygen initially present. The initial concentration of chlorocarbons was about 3300 μg/l. Results showed that the disappearance of tetrachloroethylene was accompanied by a sequential increase in trichloroethylene, cis- and trans-1,2-dichloroethylene, 1,1-dichloroethylene, and vinyl chloride (monochloroethylene). A decrease in 1,1,1-trichloroethane concentration was accompanied by an increase in 1,1-dichloroethane and chloroethane concentrations. Similarly, carbon tetrachloride degradation was accompanied by formation of chloroform and methylene chloride. Plots of tetrachloroethylene, 1,1,1-trichloroethane, and carbon tetrachloride degradation showed a linear increase with time. The biological half-lives calculated by Wood et.al. (1981) for various chlorinated contaminants are given in Table 6. It is interesting to note that the observations of Wood et.al. (1981) agree well with the results of the National Organics Reconnaissance Survey summarized by Dyksen and Hess (1982). These data show that 1,1-dichloroethane and cis-1,2-dichloroethylene occur in groundwater supplies at about the same frequency as 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene even though the latter are far more commonly used and released to groundwater.

Table 6. Biodegradation Half-Lives for Chlorocarbons by a Muck-Water Sample. (Wood et.al., 1981).

Compound	Half-life (days)
Methyl chloride	11 (Estimated)
Methylene chloride	11
Chloroform	36
Carbon tetrachloride	14
Chloroethane	10
1,1-Dichloroethane	Long
1,2-Dichloroethane	Long
1,1,1-Trichloroethane	16
1,1,2-Trichloroethane	24
Vinyl Chloride	Long
1,1-Dichloroethylene	53
Trans-1,2-Dichloroethylene	Long
Cis-1,2-Dichloroethylene	Long
Trichloroethylene	43
Tetrachloroethylene	34

Roberts et.al. (1982) studied the behavior of organic contaminants in groundwater following the injection of reclaimed wastewater at the Palo Alto Baylands, CA. Declining concentrations of several contaminants, thought to be due to biodegradation, were noticed after adsorption breakthrough. Aerobic processes appeared to be occurring since a decline in both dissolved oxygen and total dissolved carbon was noted at observation wells. Fairly rapid degradation of trihalomethanes was noted with half-lives on the order of 20 days. Much slower degradation of 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene was noted. Apparent half-lives for these contaminants were approximately 200 days. Degradation of these chlorinated contaminants appeared to follow first order kinetics. Schwartzenbach et.al. (1983) reported the behavior of organic contaminants following infiltration of river water into groundwater aquifers in the lower Glatt Valley and the lower Aare Valley, Switzerland. They observed the apparent degradation of alkylbenzenes and 1,4-dichlorobenzene, but did not notice any degradation of chloroform, 1,1,1-trichloroethane, or tri- or tetrachloroethylenes. Both aerobic processes (e.g., nitrification) and anaerobic processes (e.g., denitrification, manganese reduction) were observed at different points in the aquifers.

Bouwer et.al. (1981) investigated anaerobic degradation of several organic contaminants including chloroform and tri- and tetrachloroethylenes. Laboratory batch experiments were conducted using 1670 ml serum bottles containing an anaerobic medium which was seeded with methanogenic bacteria. Chlorinated compounds were present at concentrations from 10 - 100 μg/l. Chloroform was rapidly degraded under these conditions, but there was no appreciable degradation of the other chlorinated materials over the 16 week study period. Further work by Bouwer and McCarty (1983a) involved the same substrates at up to 200 μg/l incubated with laboratory digester sludge at 35^{o}C. Excess acetate was added to serve as the primary nutrient. Continuous flow experiments were also conducted in upflow columns containing glass beads. A biological film was established in the columns using a feed containing approximately 1 g/l of sodium acetate. The columns were then switched to a feed containing chlorinated organic compounds (including chloroform, 1,1,1-trichloroethane, and tetrachloroethylene, 160 μg/l each), with 0.5 g/l acetate as a primary substrate. The results of the batch study showed complete degradation of chloroform after a very short acclimation period. 1,1,1-Trichloroethane and tetrachloroethylene showed almost complete destruction after 8 weeks, though a longer acclimation period was required. Trichloroethylene was observed after 8 weeks as an apparent degradation product of tetrachloroethylene. The column study showed significant removal of chloroform, 1,1,1-trichloroethane, and tetrachloroethylene after 10 weeks of acclimation. The rate of degradation was observed to be more a function of the organism concentration than of the rate of acetate utilization. Reductive dehalogenation was proposed as the degradation mechanism for chloroethenes. Bouwer and McCarty (1983b) performed similar experiments under anaerobic conditions with a variety of chlorinated and brominated aliphatic compounds, using ethanol and nitrate as primary substrates. No degradation of chloroform or 1,1,1-trichloroethane was noted, but carbon tetrachloride and brominated methanes did degrade. The kinetics of biofilm transformations of chlorocarbons during laboratory simulations of groundwater flow were examined by Bouwer and McCarty (1984). A primary substrate (acetate) was found to assist in the bioconversion of a series of chlorinated aliphatic and aromatic compounds. Tracer experiments with ^{14}C-labeled substrates demonstrated anaerobic conversion of chloro-, 1,3- and 1,4-dichlorobenzenes to carbon dioxide, eliminating from consideration one possible formation route for vinyl chloride discussed previously. Further information on these anaerobic biofilm conversion experiments can be found in Bouwer's thesis (Bouwer, 1983). The aerobic degradation of chloroform and tri- and tetrachloroethylenes was studied by Bouwer et.al. (1981). One laboratory column containing granulated activated carbon and one containing glass beads were fed a nutrient medium containing sodium acetate as the primary nutrient, together with 10 - 30 µg/l of chloroform, 1,1,1-trichloroethane, or tetrachloroethylene. Aerobic growth was maintained for two years, but no degradation of any of the chlorinated contaminants was noted. Tabak et.al. (1981) also conducted studies to determine the aerobic treatability of organic priority pollutants in municipal treatment plants. The study employed a static culture flask-screening procedure in which contaminants were spiked into a yeast extract nutrient medium which was seeded with primary sewage and incubated for 28 days. Contaminant concentrations used were 5 and 10 mg/l. Blanks were run to account for the volatilization losses of volatile contaminants. Methylene chloride and carbon tetrachloride underwent slow degradation under these conditions. Considerable acclimation periods were required for degradation of 1,1-dichloroethane and 1,2-dichloroethane, 1,1,1-trichloroethane, and 1,1,2-trichloroethane. No biological degradation of 1,1,2,2-tetrachloroethane was noted and no attempt was made to identify possible biodegradation mechanisms.

Laboratory studies of the biological degradation of a number of hazardous organic compounds were reviewed by Kobayashi and Rittman (1982). They reported that the critical step in biodegradation of many chlorinated organic compounds (including 1 and 2-carbon aliphatics) appears to be reductive dehalogenation (i.e., replacement of Cl by H). This process would be favored only under anaerobic conditions where there is not a more energetically favorable electron acceptor (i.e., free oxygen) available. Reductive dehalogenation appears to be carried out by the membrane-embedded electron transport chain of whole cells, but will occur with soluble electron transfer mediators (flavins, flavoproteins, hemoproteins, cytochromes, etc.) isolated from a variety of organisms.

Parsons et.al. (1983, 1984) found that surface water and subsurface muck actively degraded tetra- and tri- chloroethylene, 1,1,1-trichloroethane and carbon tetrachloride. They incubated muck and surface water samples anaerobically with small amounts of the polychloroethylenes. About 67% of the tetrachloroethylene was degraded over a 2 week period. At the same time there was an increase in the amounts of trichloroethylene, cis- and trans-dichloroethylene, chloroethene (vinyl chloride), and dichloromethane present. The amounts of chlorinated organics observed after three weeks was less than that which was present initially. Besides loss of chlorine there was also a loss of carbon, indicating that other metabolites must also be formed. This data did not define the relationship between tetrachloroethylene and trichloroethylene degradation products. Kleopfer et.al. (1985) examined the degradation of trichloroethylene and found that under anaerobic conditions, trichloroethylene can be converted to 1,2-dichloroethylene but not to 1,1-dichloroethylene. Their experimental techniques did not differentiate between cis- and trans- forms of 1,2-dichloroethylene, however. Recent work by Barrio-Lage et.al. (1986) demonstrated the conversion of tetrachloroethylene sequentially to trichloroethylene and then to a mixture of all three possible dichloroethylenes, terminating with vinyl chloride. The sum of the products formed, however, did not account for all of the substrate removed, indicating the existence of other conversion mechanisms which do not terminate in vinyl chloride. These conclusions were confirmed by Vogel and McCarty (1985), using ^{14}C-tetrachloroethylene. There was considerable mineralization of vinyl chloride to carbon dioxide during these experiments. This result indicates that there may be a possibility for enhancing the biotransformation of vinyl chloride by adding a primary nutrient to groundwater (and possibly to landfills), a subject which was explored during a recent seminar (McCarty, 1986).

The evidence summarized above indicates strongly that a major route for formation of vinyl chloride in landfills is the anaerobic dechlorination of tri- and tetrachloroethylenes. In view of this it is worthwhile to summarize what is known of the ability of anaerobic bacteria to degrade organic materials.

The conversion of more complex organic material to methane and carbon dioxide is termed anaerobic digestion. The overall process consists of a large number of reactions, each carried by a different organism or set of organisms, forming what is defined as an anaerobic consortium. In the breakdown of cellulosic or other polysaccharide material, three distinct stages have been identified in the overall conversion process. In the first stage, complex polysaccharides are hydrolyzed into their component sugar units, which are then fermented to simpler compounds -- mainly low molecular weight organic acids. The major acid components found are acetic, propionic, and butyric acids, with minor amounts of formic, valeric, isovaleric, and caproic acids frequently found. Transitory intermediates in acid formation, ethanol and lactic acid, are converted to acetic and propionic acids, respectively. The second stage of the conversion process is the production of acetic acid from the other intermediate acids by bacteria termed acetogens. Acetogens also utilize one carbon compounds such as methanol, converting it to acetic and/or butyric acids. Methanol is produced during the breakdown of lignin. Although certain acetogens will produce butyric acid as well as acetic acid, others produce acetic acid from butyric acid with the concomitant production of hydrogen and carbon dioxide. Some acetogenic organisms will use monosaccharides such as glucose or fructose to produce acetate directly. The third stage in anaerobic digestion is the production of methane and carbon dioxide from acetate by methanogens. Other methanogens will reduce carbon dioxide to methane using hydrogen as the reductant.

One problem with anaerobic digestion to produce methane is that the acid-generating microbes prefer an acidic pH and methanogens prefer a pH between 6.2 - 7.8. The pH incompatibility of the two types of organisms can cause methanogenesis to be cyclically active in an anaerobic consortium. Temperature is another important parameter for methanogenesis. Methanogens fall into two classes with regard to preferred temperature: 30-38^{o}C for mesothermophiles and 45-60^{o}C for thermophiles (McCarty, 1964). Methanogens require a typical assortment of metal ions for growth and metabolism and about a 30:1 ratio of C:N. A source of phosphate and nitrogen are also required (Wolfe, 1971).

Based on the literature, the involvement of anaerobic digestion bacteria in formation of vinyl chloride from chlorocarbons is highly probable. Identification of which class of organism is primarily responsible would be a significant advance. Identification of individual species could then follow.

List of Probable Vinyl Chloride Emission Sources.

The primary purpose of this survey was to permit tentative identification of the most likely sources of vinyl chloride pollution. Our experimental work was designed to test the various hypotheses with a view to confirming the most important routes.

It is apparent from the foregoing, that if vinyl chloride is not initially present as an important landfill chlorinated compound, that it is formed biologically from the anaerobic dechlorination of tetra- and trichloroethylenes. Indeed, in terms of amounts produced or emitted from a landfill site, the biological route is more likely to produce greater amounts than the leaching route, simply because of the volumes of solvent typically present in a landfill. Other routes appear unlikely, based on the literature. Chemical production from chlorinated ethylenes or PVC requires high temperatures and/or extreme pH, while photochemical production in the presence of air leads to oxidized products without involving vinyl chloride as an intermediate. Thus we are only listing two sources of vinyl chloride as in any way likely, although experiments were performed to confirm the absence of other mechanisms. The likely sources are:

1. Biological dechlorination of chloroethylenes

2. Leaching

There are subsets of these two mechanisms which would be worthwhile investigating. In the case of the biological route, anaerobic dechlorination appears far more likely than an aerobic route; in which case, identification of the responsible organisms as cellulolytic, acetogenic, or methanogenic would be useful. In the case of leaching, the question of origin from "old" landfill sites containing larger amounts of monomer, or from newer samples, or even by leaching from plastic film, needs to be addressed. A further question is whether all chlorinated solvents are degraded by the same route. Some indications are that chlorinated eth_a_nes may be degraded by a different process than chlorinated eth_e_nes. These questions and others which arose during development of our experimental plan will be discussed in the next section.

EXPERIMENTAL APPROACH

The following discussion of our experimental work is based on a Work Plan which was generated in consultation with ARB staff prior to beginning actual experimental work on the project. It provides the background reasoning behind the choice of experiments, which were designed to eliminate unlikely possibilities for vinyl chloride formation (pyrolysis, photolysis, etc.), leading on to the experiments designed to test more likely mechanisms (biological degradation of TCE). The designation of "likely" or "unlikely" in turn was based on the results of the literature survey presented in the previous section.

Equipment Assembly, Calibration, and Procedure Verification

Initial work consisted of equipment set-up and testing. After evaluation of various methods available for quantitative determination of vinyl chloride in gas and water samples, we decided to apply a modification of EPA method 601. This standard method uses gas chromatography, with a packed column containing 1% of SP-1000 on Carbopack adsorbent. The unmodified Method 601 suffers from two serious problems: Poor resolution of volatile components, and the inability of the column to separate *cis*- and *trans*-1,2-dichloroethylene, two biodegradation products of trichloroethylene (TCE) on the pathway to vinyl chloride.

In order to be certain that GC peaks observed did in fact correspond to the compounds identified, we decided that a simple measurement of retention time was insufficient. Therefore, we procured and installed a photoionization (PI) detector in series with the normal hydrogen flame ionization detector. The PI detector is especially sensitive to chloroalkenes such as vinyl chloride, as well as sulfur compounds, and by using the two detectors in series it was possible to improve the probability of a correct identification of an unknown peak on the GC.

For more critical experiments which were performed to show that vinyl chloride was formed from TCE, simple identification of vinyl chloride in gas and water from treated landfill material was insufficient. This is because the background level of vinyl chloride precursors was sufficient to continue generating vinyl chloride even after addition of TCE substrate. Therefore, the TCE was labeled with a non-radioactive carbon isotope (^{13}C). Formation of labeled products from the labeled TCE was taken as a conclusive identification of origin. The isotope was determined in products by mass spectrometry (MS). The GC/MS technique was also used frequently to confirm identities of peaks observed in the experiments. In one case (methanethiol) it avoided a serious error in identification, as methanethiol and vinyl chloride have similar GC retention times, and both respond well to the PI detector.

Experiments With Primary Sewage Sludge

In the work sequence originally proposed, analytical equipment was to be assembled and techniques for vinyl chloride measurement tested prior to starting work on landfill samples. Completion of this work was intended to be coincident with receipt of landfill samples from 2 sites. This sequence required the availability of a substitute material for testing and verification of analytical techniques, one which was readily available and as closely similar as possible to landfill material. Therefore, we began measurement work with a sewage sample obtained from an assumed "clean" environment, City of Richland anaerobic digester sludge. The Richland treatment plant uses a combination of aerobic and anaerobic digestion steps to treat wastes. The material used in our experiments was taken from the second stage of two in series anaerobic digestors. After bleeding off several liters of material from the recycle line of the digestor, a one-liter plastic bottle was filled and then capped, carried back to the laboratory, and then used the same day. This material is collected from a city of 30,000 with no heavy industry and no solvent manufacturing or using facilities nearby, and is primarily of residential origin. Local industry is heavily concentrated on nuclear power plant operation and waste disposal, and hence has its own segregated and remote disposal facilities.

For analysis of sewage and landfill material incubates under aqueous conditions, we used the purge-trap system described by Dressman and McFarren (1977). A series of 40 ml vials was used for each experiment, including appropriate controls and blanks. The vials were teflon-capped to avoid problems with extraction of plasticizers (mostly phthalates) from the plastic caps. The entire system was checked using standards made from purchased chlorocarbons and a diluted VC gas mixture (100 ppm of vinyl chloride in nitrogen). The purge-trap system was set up on a Hewlett-Packard 5830A GC and standards were used to confirm that we could obtain measurable response for 2 nanograms of vinyl chloride.

Using the apparatus described above, we analyzed the initial experiments performed with Richland sewage sludge containing methanol as a carbon source for anaerobic bacteria, and inoculated with various chlorocarbons. These experiments served to establish our analytical procedures and provided much useful information about the behavior of the experimental system prior to work with actual landfill samples.

Obtaining Landfill Samples

Previous work on vinyl chloride emissions has been focused on two areas: Measurement of vinyl chloride and other organic materials in groundwater from or in the air over landfill sites, and microbiological work with non-landfill material (e.g., Florida muck; (Parsons et. al.)). Since the purpose of this project was to identify the sources of vinyl chloride emissions from California landfills, it seemed important to do most of the work with actual landfill material. Under ideal circumstances, a range of landfills would have been sampled to various depths and in various locations. In order to perform the project in a reasonable time, however, we selected just two sites, and arranged with our subcontractor (Emcon Associates, San Jose, CA) to perform sampling at two locations within each site, taking two samples from each drilling at depths of 3 and 10 ft below the cover, plus surface soil. To further vary the sampling conditions, Site A was in Southern California, had been used for solvent dumping, and did have measured concentrations of vinyl chloride air emissions; Site B was in Northern California, had no history of chlorinated solvent waste dumping, and had had only traces of vinyl chloride identified in the groundwater. With these widely varying conditions we hoped to cover the spectrum of vinyl chloride production conditions (although a hazardous waste dump site was not included). The penalty for this is that with so few samples covering such a wide range, any sort of a "representative" sample could not be hoped for. In fact, samples actually obtained varied considerably in appearance. The identities of the sites selected for sampling is not relevant to the work, and one site requested confidentiality. Therefore, the two sites are simply designated A and B. These samples of landfill material were subjected to the experimental procedures described below to determine which of several classes of mechanism was responsible for vinyl chloride formation. These are: Microbial, chemical, thermal, and photochemical.

A total of 12 samples was obtained from the two sites. These were labeled at the site, and gas analysis, pH and temperature measurements were made at the various sampling locations and depths. Because of the importance of maintaining any microorganisms in a viable state, arrangements were made with the subcontractor that transfer to Battelle-Northwest would be made as rapidly as possible, at above 20^{o}C in sealed containers and in an atmosphere of landfill gas. We therefore presumed that the samples represented actual landfill site environments fairly closely on receipt. The initial measurements consisted of a void space gas analysis from each sample container (before opening in an inert atmosphere) and a microscopic examination to determine the presence of living organisms. The samples were then flushed with argon/carbon dioxide to remove residual vinyl chloride, split, and placed into vials for experimental work.

Description of Site A, Southern California

Apart from the sewage sludge sample, which was obtained from a local treatment facility, we felt it important to perform most of our work with actual landfill material, even though such material is highly heterogeneous and variable. We were able to obtain permission for sampling from two landfill operators: One in Southern and one in Northern California. Since the purpose of the sampling was to obtain research material and was not intended in any way to be a site survey, the actual locations of the sites are not important. However, because the sampling procedures may have some bearing on the results and because other researchers may wish to compare their results with ours, general site descriptions, details of sampling procedures, locations within the sites, and on-site measurements are presented here.

At Site A, in Southern California, refuse was disposed of from 1973 to 1983. Figure 4 shows the landfill shape and the sampling locations (black dots). The maximum depth of fill is ~ 135 ft. and the average fill depth is ~ 10 ft. Site A was permitted to operate as a Class III solid waste disposal facility by the California Regional Water Quality Control Board. These wastes consist of commercial and household refuse, construction and demolition debris, and non water-soluble, non-decomposable and inert solid industrial wastes. Disposal of toxic wastes and wastes with a moisture content exceeding 50% was prohibited. Most of the landfill cover soil material was derived from a conglomerate formation consisting of well-rounded siliceous gravel and cobbles in a silty sand matrix. Typically fine-grained, the matrix contains 25-30% silt and clay-sized material. The gravel and cobble inclusions range in size from 1" to over 1 ft in diameter, with an average size of ~ 3". The fine sand and silt size materials within the matrix reduce soil permeability to the 10^{-5} to 10^{-7} cm/sec range. The site is equipped with a landfill gas recovery system.

To collect samples representative of the landfill, sampling borings were located a minimum of 1500 ft apart. Three factors influenced the choice of drilling locations at this site: (1) The desire to avoid interference with potential future landfill gas recovery activity involving the gas well system, (2) the accessibility of drill rig and other vehicles to the sampling locations, and (3) the presence of active decomposition within the landfill location. Drilling locations had previously (April 25, 1986) been identified by Emcon in collaboration with ARB staff during a site visit. A portable VOC monitor was used to confirm point #(3), above.

Description of Site B, Northern California

At Site B, refuse disposal without burning began in 1973 and continues at this time. The sampling area (Figure 5) comprised ~ 6 acres with an average fill depth of ~ 30 ft. Site B is also a Class III landfill. The refuse soil cover consists of clay with silt and some gravel. The boring locations were chosen for similar reasons as for Site A, that is, (1) to collect samples as representative as possible, (2) to avoid interference with

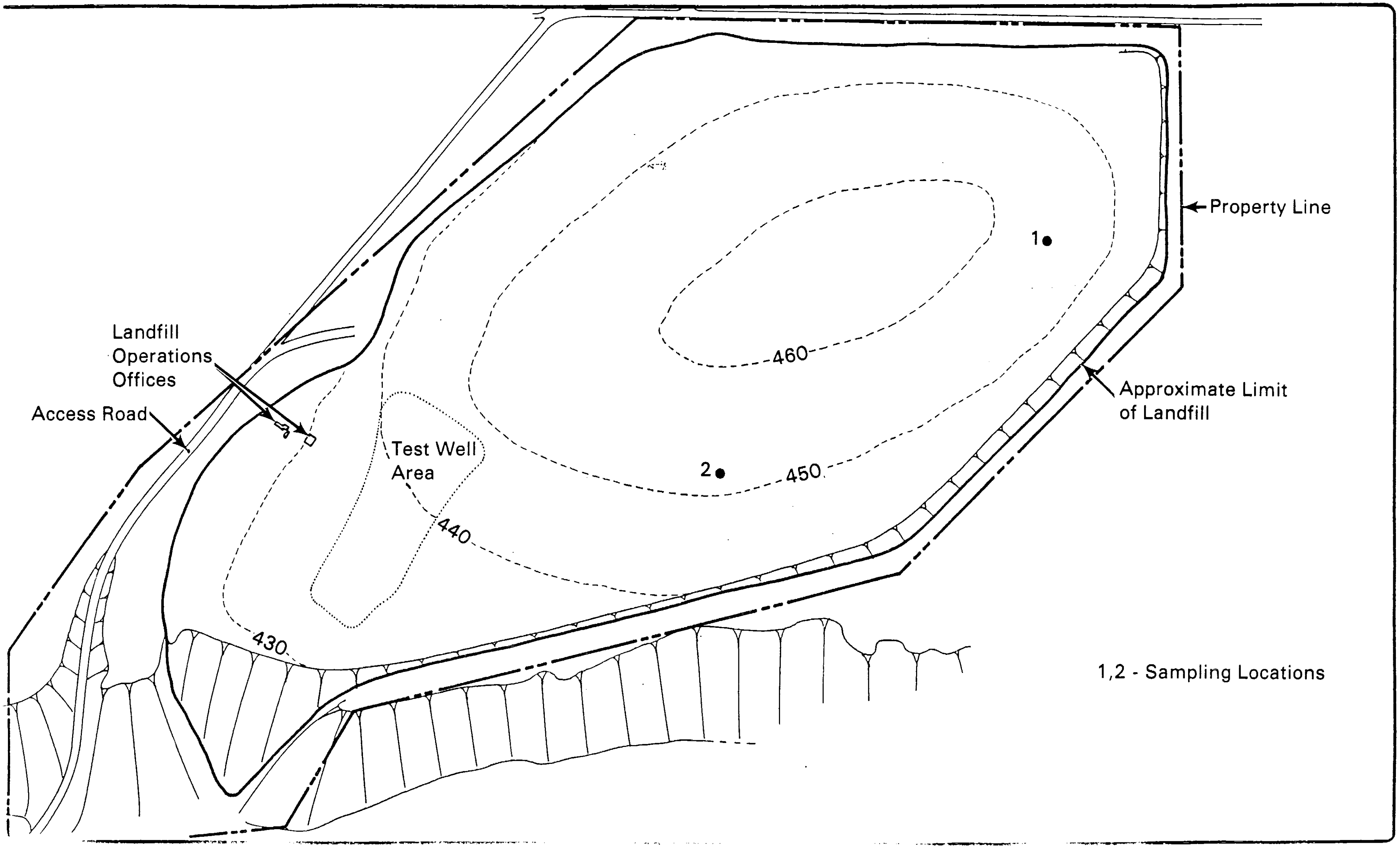


FIGURE 4. Landfill Site A, Southern California

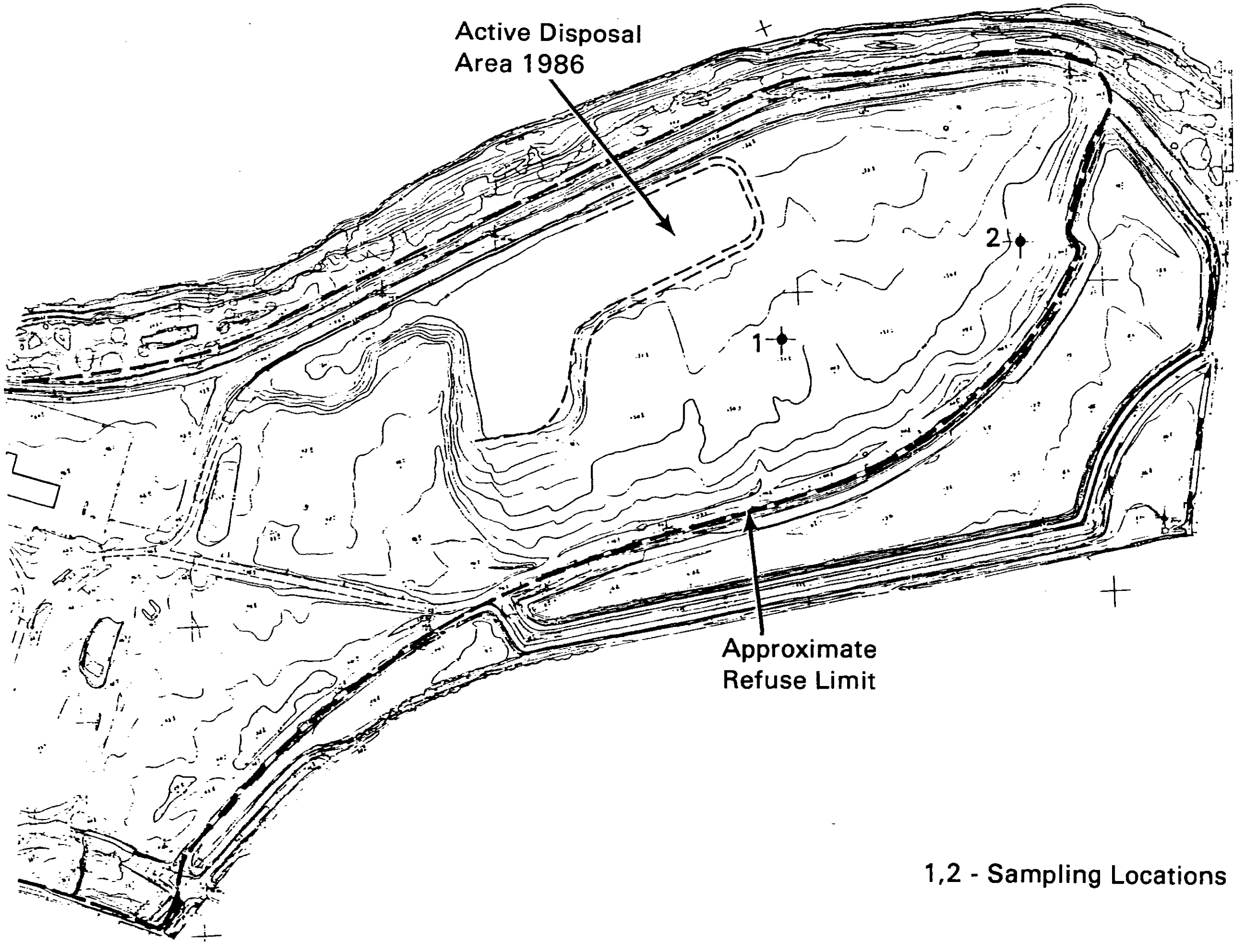


FIGURE 5. Landfill Site B, Northern California

refuse disposal activity, and (3) from an area with active decomposition of refuse occurring, as measured with a portable VOC monitor. Drilling locations were identified on May 2, 1986, by Emcon in collaboration with ARB staff during a site visit. The borings were located a minimum of 500 ft from each other and a minimum of 300 ft from the active fill area.

The samples obtained, as for Site A, included two surface soil samples, plus landfill material from depths of 3 and 10 ft. below the cover. Four gas samples taken at these depths were also obtained (the gas sample from the surface samples was included with the surface solid samples and consisted of surface air). At the time of sampling, temperature and pH measurements were also taken. Oxygen levels in the gas from buried samples was higher than the 1.2% background normally experienced, although Emcon measured zero levels at all depths. However, the Site B cover was sandier than the Site A cover, and this may reflect a higher oxygen permeability in the landfill.

Chemical Analysis of Landfill Materials

Confirmation of activity: Samples were incubated in vials without additions, for one week, with removal and analysis of a gas sample to confirm the continued production of vinyl chloride from the material.

Inorganic analysis: Approximately 2 g of each material was required for analysis of inorganic composition, including sulfur and phosphorus. Of the two techniques available at Battelle-Northwest (Inductively Coupled Plasma Spectrometry (ICP), and X-ray fluorescence spectrometry), we chose the ICP method (procedure described in Appendix C).

Organic analysis by GC/mass spectrometry: A further 10 g of each material was used for head-space analysis and identification and determination of baseline levels of chlorinated solvents in the landfill material, using the standard techniques already developed.

Irradiation sterilization samples: Approximately 10 g was taken from each active sample as determined above, for irradiation and subsequent incubation and demonstration that no vinyl chloride was produced. If vinyl chloride was still produced, it would indicate that a non-biological route for vinyl chloride production existed in the sample.

Samples for pyrolysis in inert atmosphere: About 20 g of two samples was pyrolyzed to 650°C and the evolved gases collected and analyzed by GC/MS. Because of the expected high organic content of the landfill material, a complex GC trace was expected (and obtained), with several hundred compounds present. The pyrolysate gases were analyzed for vinyl chloride and related chlorinated compounds. A further sample was 'spiked' with PVC powder (10%) and pyrolyzed similarly. The pyrolysis was performed in a tube furnace and evolved materials collected and analyzed after heating to 150, 300, 450, and 650°C. The 150°C sample was expected to contain water and most of the chlorinated solvents.

Samples for photolytic treatment in presence of TCE: To confirm extensive literature reports that photolysis of chlorinated compounds does not contribute significantly to vinyl chloride production, we subjected two samples of landfill material to UV light in the presence of ^{13}C-labeled TCE, and confirmed by GC/MS that in the presence of air there was no production of vinyl chloride. One sample was purged with inert gas prior to the addition of the labeled material and the other was photolyzed in air.

Based on the literature review already performed, we expected the above preliminary experiments to have negative results. The evidence already available clearly implicates vinyl chloride production as a result of anaerobic microorganism action on chlorinated solvents. In the event that any positive results were obtained, additional experiments would have been performed as follows:

1. Vinyl Chloride Formation from Irradiated (sterile) Samples

A positive result here could indicate a non-biological formation mechanism for vinyl chloride formation, or it could indicate radiolytic formation from other chlorinated compounds, or extracellular enzymatic dechlorination of these compounds (enzymes are generally not inactivated by this dose of radiation). To determine which is the case, a further landfill sample would have been purged with inert gas and autoclaved with 15 psi steam for 30 min., and again incubated with labeled trichloroethylene. This treatment would have inactivated any extracellular enzymes. Autoclaving itself should not produce vinyl chloride, as the expected product from trichloroethylene is a hydrolysis rather than a dechlorination product. (Lack of vinyl chloride formation from the pyrolysis experiment would have confirmed that heat alone was not responsible.) If vinyl chloride was still produced, this would have indicated a purely chemical formation route unaffected by radiation, heat, or steam, and hence likely to be a catalysis reaction. This is an unlikely result, but if it had occurred, further experiments would have been designed based on the ICP and organic compound analyses of the landfill material, plus a series of incubations of labeled trichloroethylene with pure inorganic components of the sample. These experiments would be designed to indicate if the reaction was catalytic in nature. Since a biological formation route is already clearly established in the literature, work on catalytic formation of vinyl chloride would have had to replace some biological experiments. The degree to which this would have been done would have been determined through consultation with the sponsor, as it would have involved a change in work scope and direction.

2. Vinyl Chloride Formation During Pyrolysis

Formation of vinyl chloride during pyrolysis of PVC is known, although the levels of vinyl chloride produced are low (several ppm maximum). The only rational way for vinyl chloride to be formed during pyrolysis of landfill material is through local combustion. It is possible to make a rough calculation of the maximum theoretical amount of vinyl chloride that could be produced in this way, from analysis of carbon and chlorine contents of the landfill sample. Theoretically, pure PVC could depolymerize to 1 million ppm of vinyl chloride; in practice, no more than 6 ppm has been found after anaerobic pyrolysis and 35 ppm after pyrolysis in air. Taking the higher value, assuming that all carbon in the landfill sample is in the form of PVC, and that no other gaseous products are formed (even excluding methane and carbon dioxide), 1 ppm of vinyl chloride would be formed if there were 1/35 of the total landfill sample in the form of PVC (2.9%). This is equivalent to 1.12% carbon. Where the calculation falls down is in the assumption that there is no air flow over the landfill and that all gases are collected - the 1 ppm vinyl chloride value is the total formed in a closed system if all of the PVC decomposes in a very short time. Any air movement will dilute the vinyl chloride, as will any formation of methane and carbon dioxide. Hence it is unlikely that the observed vinyl chloride levels (maintained over a period of years) are due to PVC decomposition. This can be shown easily if the measured landfill sample temperatures are initially below about 400°C, below which temperature vinyl chloride formation from PVC is insignificant. This turned out to be the case.

Formation of vinyl chloride by pyrolytic dechlorination or dehydrochlorination of organic solvents is a further possibility, and could involve catalysis by inorganic components of the matrix. If we had observed vinyl chloride formation in excess of that expected from PVC pyrolysis, this possible mechanism would have been checked by 'spiking' landfill samples with individual solvents and pyrolyzing them.

3. Formation of Vinyl Chloride During Photolysis

If vinyl chloride had been formed during aerobic photolysis of a landfill sample containing ^{13}C-labeled trichloroethylene, the experiment would have been repeated (a) anaerobically, (b) with variations in trichloroethylene concentration, (c) with photolysis times of 1-12 hr., and (d) with other solvents including (unlabeled) tetrachloro- and dichloroethylenes and tetrachloroethane.

The experimental matrix was continued with the assumption that vinyl chloride is not formed by radiolysis, pyrolysis, or photolysis. The available evidence strongly supports a biological formation route for vinyl chloride, from dechlorination of chlorinated solvents by anaerobic microorganisms.

Microbial Metabolism Experiments

Anaerobic bacteria are responsible for the fermentation of organic wastes containing cellulose to methane and carbon dioxide; they are also capable of generating a wide variety of other compounds *en route* to methane. In general they consist of three types: Those which degrade cellulose to glucose and related compounds, those which take the fermentation further to acetic acid (acetogens), and those which decarboxylate acetic acid to methane (methanogens). Each type has its own range of discrete organisms with its own growth requirements, which are not always compatible. Also, some organisms enter into a kind of interdependence whereby an excreted product from one becomes necessary for the growth of another. Although a great deal of work has been done on the classes of anaerobic bacteria, there is still much to be learned about their nature and mode of action. Of particular relevance to this project is their ability to anaerobically dechlorinate TCE and other solvents to vinyl chloride. Hence, one of the goals of the project was to attempt to isolate and identify one or more of the vinyl chloride-producing anaerobes present in landfill material, after first demonstrating that anaerobic organisms are in fact responsible for vinyl chloride production in the landfills. From the above comments it can be seen that this is by no means an easy task. In order to achieve the project goals, beginning with proof of biological formation of vinyl chloride, we decided on the following experimental approach:

1. Set Up a Standard Inoculum of Microorganisms for Biological Experiments

A stock culture of anaerobes derived from sewage sludge or landfill material was necessary to ensure uniformity in performing microbial incubation experiments. Ideally, the inocula for different experiments should contain the same number of the same species of organisms per unit volume of inoculum. This was achieved by maintaining a stock culture in a 2 liter fermentor.

2. Use Sewage Sludge to Test Experimental Methods and to Show Vinyl Chloride Formation

A description of the use of City of Richland sludge to test experimental methodology has already been given. As part of these experiments, we incubated Richland sludge with various chlorinated solvents and labeled TCE to determine whether or not vinyl chloride was formed. A positive result from these experiments indicates that the ability of anaerobic microorganisms to form vinyl chloride is (a) ubiquitous, and (b) constitutive in these bacteria, because it may be assumed that these organisms had never been exposed previously to significant amounts of chlorinated organic compounds.

This preliminary work was designed to provide information on whether or not vinyl chloride can be formed from TCE by common anaerobes, and whether adaptation and prior exposure to solvents is necessary for activity. We hoped thus to confirm the mechanism which appears from the literature to be of primary importance in vinyl chloride formation. We also hoped to learn which of the three primary classes of anaerobic bacteria (hydrolytic, acetogens, or methanogens) are responsible for the conversion, by enrichment on glucose or methanol as carbon sources.

3. Incubation of Landfill Materials with Solvents

Experiments similar in scope to those to be carried out using Richland sludge were planned for landfill material. These experiments were to be carried out using a standard inoculum containing mixed landfill organisms maintained on glucose or methanol in the presence of 200 ppm of one of a series of various chloroethenes including tetrachloroethylene, TCE, and dichloroethylenes. A standard procedure for these experiments is described in the next section. Generally, these inoculated vials (termed "microcosms" in the literature) were incubated at 35 or 55°C for 1-6 weeks, and the vinyl chloride and other chlorocarbon materials determined by the purge-trap method. Use of labeled TCE as a substrate permitted confirmation of labeled vinyl chloride formation in critical experiments.

Characterization of Vinyl Chloride-Producing Organisms

Initial work with sewage organisms was intended to permit us to determine the nutritional and physical requirements for chloroethylene degradation. Temperatures of 45-60°C and 30-38°C favor different groups of anaerobic organisms. Both temperatures are possible in landfills, the higher value being typical of freshly fermenting material, and the lower typical of established volumes where most of the cellulosic material has already been converted. Carbon in these experiments was supplied as methanol or acetate. Glucose will support a food chain of all three general types of anaerobes. Methanol will support a food chain of acetogens and methanogens, and acetate will support methanogens only.

An attempt to isolate the microorganisms responsible for vinyl chloride formation was included in the planned work, because of its importance, although it is a difficult procedure and somewhat "open-ended". Standard microbiological procedures will allow isolation of anaerobes, which sometimes can be identified as previously known species. However, these experiments are time-consuming, and subject to interruption from unknown factors which may cause cultures to fail to grow, or to "crash" after initial growth. Organisms in anaerobic environments are generally delicate and much less well understood than aerobic equivalents. The procedures followed are summarized thus: Plating sample cultures onto Petri dishes allows individual organisms to be separated. Petri dishes were incubated anaerobically using an anaerobic GasPak system. This system is preferred over an anaerobic incubator because it allows stacking of 10-15 plates in an individual container; observations can be made without disturbing the atmosphere over other experiments as would occur with a larger incubator. Also, this system offered a choice of using a pure carbon dioxide or a mixed carbon dioxide/hydrogen atmosphere. These small units can be filled inside an anaerobic glove bag to avoid air contamination, and then removed to the constant temperature incubator. Individual microbial colonies can be cultured separately and these cultures then screened for the ability to degrade chloroethylenes. Microscopically unique isolates found to degrade chloroethylenes can be typed using the procedures in Bergey's Manual of Determinative Bacteriology. If we found several organisms which could degrade chloroethylenes then a large number of isolates would have had to be examined microscopically or by biochemical tests to give an idea of the population distribution of active anaerobes in the samples.

Initial experiments were performed with landfill sample microbial isolates to determine their temperature range (thermophilic (45-60°C) or mesophilic (30-38°C) and metabolic type (cellulose-degrading, acetogenic, or methanogenic). The temperature of the samples removed from the landfill was measured at the time of landfill sampling. Subsequent incubation of the samples with labeled TCE allowed correlation of vinyl chloride formation with specific sample temperatures and carbon sources. Streaking and individual colony isolation of single species was then attempted on agar plates. Incubation of colonies thus isolated with labeled TCE allowed us to define which isolates showed activity in producing vinyl chloride. These isolates were then cultured in liquid media to obtain information on their nutritional requirements. Because of the amount of work involved in this portion of the project, and the difficulty of estimating time required (due to the wide range of microorganism characteristics in landfill material) an accurate prediction of how many organisms could be isolated and identified was not possible. We hoped to identify 2-3 of the major contributors to vinyl chloride production, with growth on two defined published media. Detailed nutritional studies on these organisms were beyond the scope of the project. One interesting question that can potentially be answered using an anaerobic reactor and a defined inorganic medium is whether or not the organism uses chloroethylenes for energy metabolism or as a carbon source for growth. In the latter case, the organism(s) can rather easily be isolated by enrichment on a mineral salts medium containing a chloroethylene. Initially, a good carbon source is added (e.g., acetate), and this is gradually depleted until only the chloroethylene is available as a carbon source. An aliquot of a growing culture is added to a continuous fermentor under conditions where only growing organisms are maintained. The dilution rate is then gradually increased until washout of the cultured organism begins to occur. At this point the dilution rate is stepped back to the last stable value and held until equilibrium is achieved. The organism metabolizing chloroethylene will thus have been isolated, or at least significantly enriched. The organism can then be typed.

The above experimental approach for isolating vinyl chloride producing organisms was followed initially. Subsequent experimental work though led us to modify our techniques. The most important of these changes was the use of the roll-tube technique for the growth and isolation of strict anaerobes for isolation of single microbial colonies. A second modification was in the use of a stirred tank reactor to maintain anaerobic organisms at high levels for experimental work. Neat methanol was added to the reactor and gas formation monitored to maintain the organisms and determine their state of vigor. Details of experimental procedures used to perform the experiments outlined above are presented in the next section.

MATERIALS AND METHODS

Material Sources, Composition, and Purity

Vinyl Chloride: Cylinders containing 1, 10, and 100 ppm vinyl chloride standard gas in nitrogen were obtained from Scott Specialty Gases (Ann Arbor, MI). The manufacturers' analysis is reproduced below:

Mixture 70	0.9917 ppm VC
Mixture 71	10.02 ppm VC
Mixture 73	100.4 ppm VC

Accuracy of the analysis was +/- 2%, traceable to NBS standards. The purity of the vinyl chloride in this standard gas mixture was confirmed by purge-trap analysis and GC/MS analysis of the purged (concentrated) product.

Chlorocarbon Standards: These were obtained individually from Aldrich (Milwaukee, WI), and were of the highest purity available commercially (Gold Label grade). To check on calibrations for purge-trap analyses, standard mixtures of chlorocarbons were obtained from Alltech Associates (Deerfield, IL), and Supelco (Bellefonte, PA). The composition shown in Table 7 is of the standard mixture.

Water: Water used in all experiments was deionized in our laboratories and was free of organic compounds, with a conductivity of >16 Megohm-cm. It contained no chlorocarbons to the limit of our instrument sensitivities, as determined by a purge-trap analysis of a water blank. The water was autoclaved for 15 min at 15 psig of steam for use as sterile water.

Site Sampling Procedures

Sampling requirements were specified as follows: At each of two locations at each site, one sample of cover soil and two landfill material samples were to be taken, together with associated gas, and measurements of pH and temperature. The landfill samples were to be as close to 3 and 10 ft below the cover, respectively, as possible, and were not to consist of a single material (e.g., rock or paper). In total, two soil samples, four refuse samples, and four gas samples were to be obtained at each site. This plan was followed for both sites, but practical difficulties made some variations inevitable.

Table 7: Components in Purgeable Halocarbon Mix 60/M2, Lot LA 13373.

Compound	Concentration (mg/ml)	~ R_t(Lit.) (min)
Dichloromethane	0.60	6.6
1,1-Dichloroethylene	0.12	8.5
1,1-Dichloroethane	0.12	9.5
Trans-1,2-dichloroethylene	0.12	10.1
1,2-Dichloroethane	0.12	11.2
1,1,1-Trichloroethane	0.12	12.0
Tetrachloromethane	0.12	12.6
1,2-Dichloropropane	0.12	14.0
Trans-1,3-dichloropropylene	0.19	14.0
Trichloroethylene (TCE)	0.12	14.6
Cis-1,3-dichloropropylene	0.05	15.0
1,1,2-Trichloroethane	0.12	15.0
1,1,2,2-Tetrachloroethane	0.12	19.0
Tetrachloroethylene	0.12	19.0
Chlorobenzene	0.60	21.5
1,2-Dichlorobenzene	0.60	22+
1,3-Dichlorobenzene	0.60	22+
1,4-Dichlorobenzene	0.60	22+

\+ Stock # 4-8747.

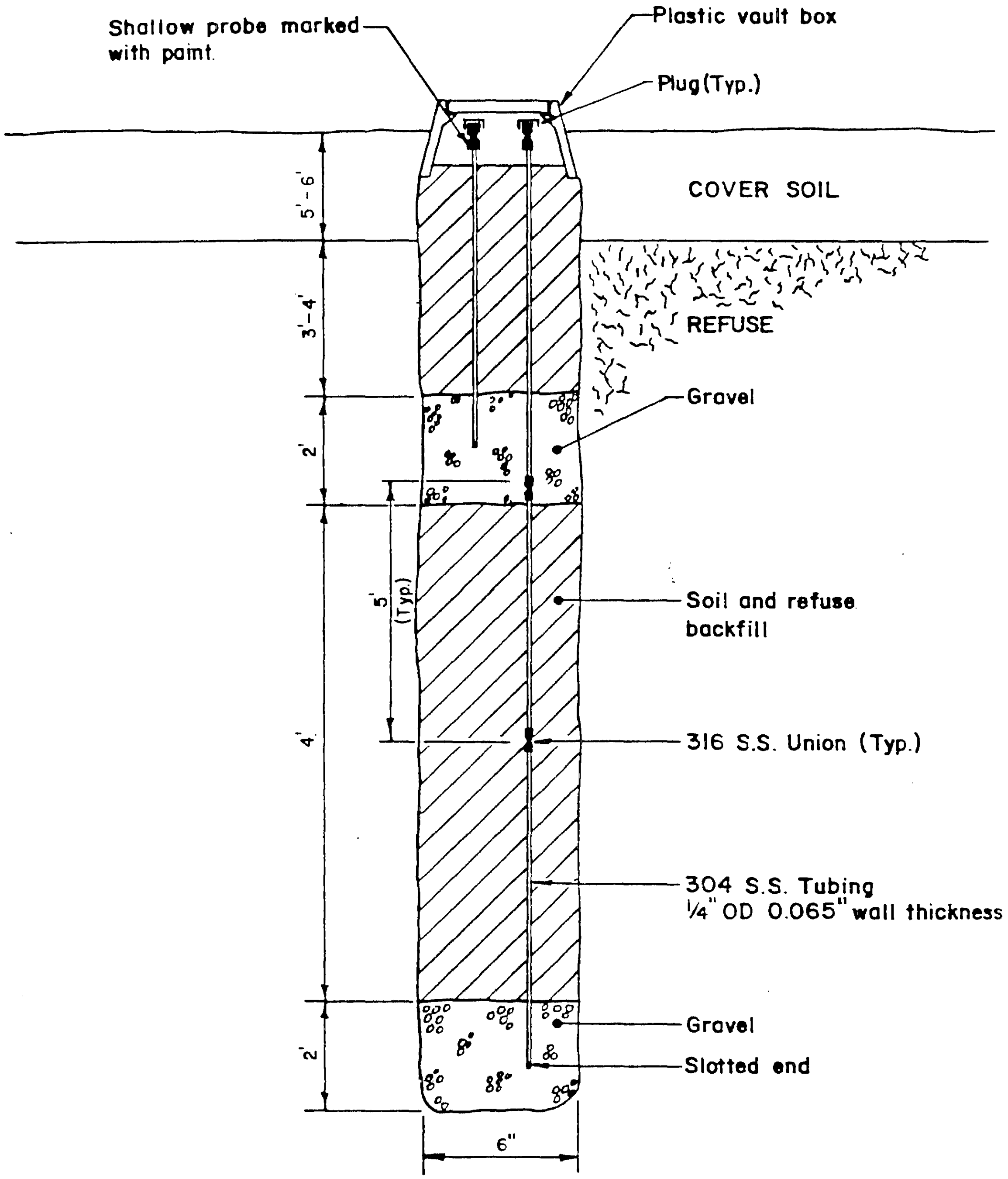
1-^{13}C-Trichloroethylene (1-^{13}C-TCE, 100 mg) was obtained from Merck, Sharp, and Dohme (Quebec, Canada).

A CME 550 All-Terrain model drill rig with a 6" solid-flight auger was used to collect cover soil and refuse samples. The augers and bit were steam-cleaned before each borehole was drilled. The cover soil samples were collected from the flights of the auger as soon as the cover layer was penetrated. The temperature of the cover layer at the refuse/cover interface was measured with an Electrotherm SH44 digital thermocouple sensor, pre-calibrated against a standard mercury thermometer, and the cover thickness recorded. Drilling then proceeded to the first refuse sampling point, at ~ 3ft. depth. The auger was retrieved and a refuse sample collected with a split-spoon sampler, which collects a sample from a refuse interval of ~ 18". The sampler also protects the sample from excessive aeration after retrieval. To provide an oxygen-free environment for the sample after retrieval the sample was immediately placed in a bag filled with landfill gas (55% CH_4:45% CO_2)

collected from the landfill gas test well system. The sampling procedure was chosen to minimize disturbances to the native anaerobic bacteria in the refuse by either oxygen infusion or high temperatures. Generally, a few seconds exposure to air is not considered harmful to most anaerobic species; also, collection of a solid from a tube bore sample keeps most organisms covered and thus protected from air during the short time required for transfer to the anaerobic environment of the sample bags. After the first sample was taken, a second refuse sample was retrieved from the boring immediately below the refuse sampling location, for measurement of pH. A Hach model 17200 portable pH meter was used, after calibration in the field with pH 4 and pH 7 solutions. The temperature at the bottom of the boring was then measured using the digital thermocouple sensor. After the refuse sample was obtained at the first sampling point, drilling was resumed until the second sampling point was reached, where the sampling procedure was repeated.

After refuse samples were collected, the resulting borehole was used to collect gas samples. Gas monitoring equipment used on-site consisted of a Gastech GX-3N instrument, with a capacity for measurement of combustible gas in the 0-5 and 0-100% ranges, and oxygen in the 0-25% range. It was precalibrated against 45% methane/55% carbon dioxide. Gas sample bottles at Site A were Whitey 1000 ml 304 stainless steel cylinders with Whitey 14-DKM 454 316 stainless steel shut-off valves. The manufacturer's data states that these cylinders were cleaned with TCE before shipment. To ensure cleanliness, the cylinders and valves were triple-rinsed with TCE and heated for 60 hr at 105^{o}C to remove any solvent residue. At Site B, due to a late delivery of the gas sample cylinders from Site A to Emcon, different sampling cylinders were used. These comprised 3 Whitey 200 ml sampling cylinders with the same specifications described above, and 5 Kildee Scientific 500 ml glass sampling bottles. Approximately 2 ft of gravel was placed at the bottom of the boring, then a gas sampling probe tube was inserted into the boring to permit collection of a gas sample at the deeper location. The gas sampling probe is shown in Figure 6. It consisted of 1/4 in 304 stainless steel tubes with a 0.065 in wall thickness, in 5 ft sections coupled with 316 stainless steel unions. After gas sample collection, the hole was then backfilled with cover soil to the elevation of the first refuse sample, where additional gravel was placed and the gas sample at 3 ft depth obtained.

FIGURE 6. Gas Sampling Probe



NOT TO SCALE

d.a.e. 5/86

EMCON Associates
San Jose, California

BATTELLE NORTHWEST LABS
VINYL CHLORIDE LANDFILL METHANE
RECOVERY ASSESSMENT STUDY

GAS SAMPLING PROBE CONSTRUCTION

PROJECT NO.
494 – 03.01

Gas samples were collected by connecting a 1000 ml stainless steel or glass gas sampling bottle directly to the sampling tube and then purging the sampling bottle. Purging continued until the methane content reached a consistent value as indicated by portable gas monitoring equipment. Duplicate samples were collected. The gas samples did not contact any plastic material after entering the stainless steel sampling tube.

A plastic vault box was installed over the sampling tubes for protection in the event that additional gas samples were required. The location of the boxes on the site was clearly marked with lathe and marker tape.

All equipment was cleaned and calibrated before sampling, as described above.

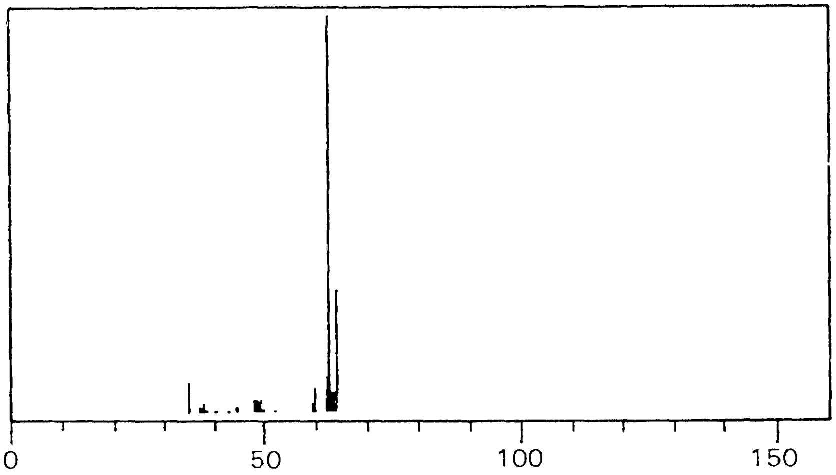
Laboratory Instrumental Analysis Systems:

Gas Chromatography: A Hewlett-Packard 5830A instrument was used for gas chromatography. It was fitted with a photoionization (PI) detector in series with a flame ionization detector (FID). The PI detector was obtained from HNU Systems, Inc. (Newton, MA). Tubing connections were 1/16 in diameter deactivated stainless steel to minimize void volume between the column exit and the detector chambers. Initial work was performed using the EPA 601 method, which requires a packed glass column (180 cm x 4 mm i.d.) containing 1% SP-1000 (60-80 mesh) on Carbopak B. This column diameter was used for purge-trap analyses; for direct injection analyses, a similar column but with an i.d. of 2 mm was used. A 180 cm x 4 mm glass column packed with 1/3 Chromosorb 101 and the remaining 2/3 with Chromosorb 102 was used for all subsequent analyses. This column gave good resolution of volatile compounds and separated <u>cis</u>- and <u>trans</u>-1,2- dichloroethylenes. Temperature and flow conditions were as follows: Initial, 50^{o}C for 0 min, programmed at 10^{o}C/min to 180^{o}C; held for 20 min.

Mass Spectrometry: A Hewlett-Packard 5992 GC/MS combination with an all-glass jet separator was used for GC/MS work. The GC was fitted with a 180 cm x 2 mm i.d. Chromosorb 101/102 column. A sample spectrum of vinyl chloride standard injected into this system is shown in Figure 7.

Figure 7: Mass Spectrum of Vinyl Chloride Standard.

Retention Time = 4.8 minutes
Scanned from 33 to 200 amu
Number of Peaks Detected = 20
File Type = Linear
Base Peak=61.90
Base Peak Abundance=349
Total Abundance=674



Lower Abundance Cutoff Level = 0.0%

Mass	Abundance (%)	Mass	Abundance (%)	Mass	Abundance (%)
34.90	7.7	46.80	4.0	60.90	9.7
35.90	2.3	47.90	3.7	61.90	100.0
36.90	3.4	48.90	4.0	62.90	5.7
37.80	1.1	49.90	2.3	63.90	30.9
39.90	1.4	50.90	0.9	83.80	0.3
41.80	0.9	58.90	2.9	85.80	2.3
43.90	2.0	59.90	7.4		

Purge-Trap Apparatus: A diagram of the purge-trap apparatus is shown in Figure 8. This is similar to the apparatus described by Bellar et.al., (1976). Operating procedure was similar to that described by Dressman and McFarren (1977). The packing for the trap used in the apparatus was modified somewhat to allow efficient trapping of vinyl chloride and elution of higher molecular weight chlorocarbons. Experiments with Tenac, Sperocarb (charcoal), or silica alone showed that none of these packings by itself would give the desired retention times. A 7 cm length of Tenac backed by a 7 cm length of charcoal was finally selected as the optimum. Operation of the purge-trap assembly was as follows (with reference to Figure 8): The purge assembly was mounted and system pressure released by actuating the three-way valve A. After insertion

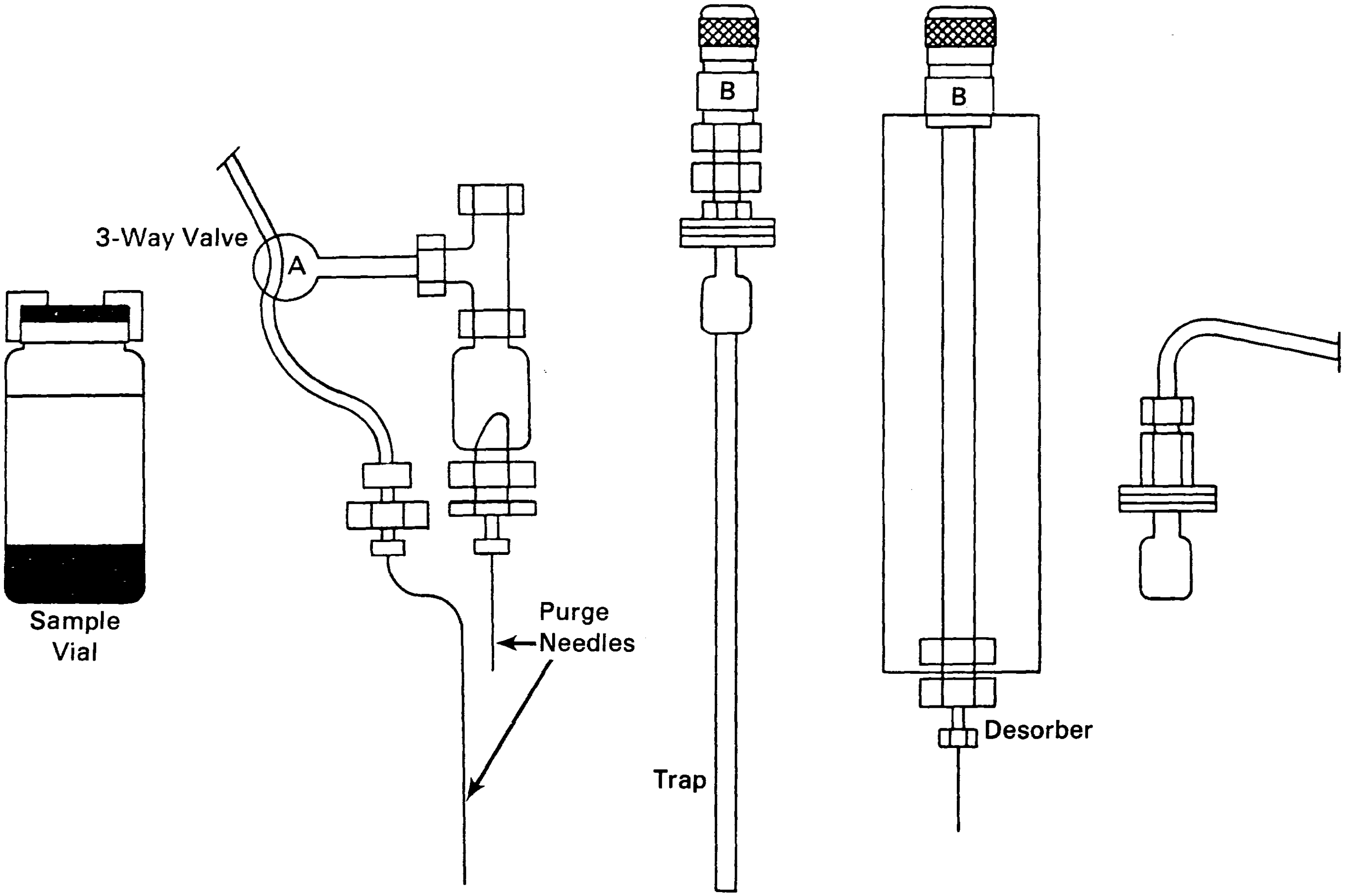


FIGURE 8. Schematic of Purge-Trap Apparatus

of the gas purge needle into the sample vial (a standard 40 ml septa cap vial with ~ 10 ml head space), the three-way valve was turned to the purge position and a flow of 60 psi nitrogen was maintained at 20 ml/min for 10 min, to carry the volatiles into the trapping column. The purge nitrogen was a prepurified grade further purified by a molecular sieve drying trap. It contained no detectable chlorocarbons as determined by purge-trap analysis of a blank sample. The third position of the three-way valve is for post-purge, performed in order to remove excess water. Post-purge was not necessary when the Chromosorb 101/102 column was used. After absorption the head pressure on the column was reduced to zero and the septa quick-disconnect (B) was disconnected. The purge-flow assembly was then mounted on the GC. Pressure on the desorber flow gas was vented by pressing the button on the quick-disconnect, which was then attached to the purge-trap. Desorption of vinyl chloride onto the GC column was achieved by a 3 min elution at 150°C, with a 60 psi, 20 ml/min carrier gas flow. During this period the GC column was maintained at room temperature. The oven door was closed and both detector integrators turned on. The water peak appeared first (negative peak on the PID). The trapping apparatus was then reconditioned for the next run. This was achieved by heating for 30 min at 180°C with a flow of 20 ml/min of nitrogen.

The efficacy of the purge-trap technique for vinyl chloride analysis was determined to be 100 +/- 2%, using pure water standards. Chlorocarbon standards were prepared at the same concentrations as used in incubation experiments. Spike solutions were prepared by dilution of 100 mg of the test compound in 10 ml of pure methanol. The actual concentrations resulting are given in Table 8, together with GC retention and GC/MS peak data.

For the analysis, a ~ 10 μl sample of the diluted chlorocarbon was added to ~ 30 g of ultrapure water in a 40 ml septum-capped vial. Negative peaks on the resulting GC traces at 2.5 and 4.9 min were from water and methanol, respectively. The GC column (see above) was packed with Chromosorb 101/102, which separates vinyl chloride from the water peak and also separates all 3 dichloroethylene isomers.

Table 8: Chlorocarbon Standard Solution Concentration and Analytical Data.

Compound	Concn. (µg/ml)	GC/MS R_t (min)	Ions Used (m/e)	GC PID/FID R_t	
				Col. 1*	Col. 2
Vinyl Chloride	0.031	5.1	62,64	6.5	2.1
1,1-Dichloroethylene	12.43	9.2	61,96,98	10.7	7.8
Trans-1,2-Dichloroethylene	9.18	10.3	61,96,98	11.7	9.9
1,1-Dichloroethane	9.73	11.1	63,65,83	12.6	9.1
Cis-1,2-Dichloroethylene	10.28	11.3	61,96,98	12.8	9.9
1,2-Dichloroethane	11.06	12.8	62,64,98	14.4	11.2
1,1,1-Trichloroethane	10.89	12.9	61,97,99	14.8	12.3
Trichloroethylene	10.81	13.6	95,97 130,132	15.6	15.3
1-^{13}C-Trichloroethylene	7.09	13.6	96,98 131,133	15.6	15.3
1,1,2-Trichloroethane	11.68	16.3	83,97,99	20.8	16.0
Tetrachloroethylene	11.05	16.8	129,131 166	21.0	20.8
1,1,2,2-Tetrachloroethane	12.41	>30	83,85,168	33.3	20.8

* Column 1, Chromosorb packing; Column 2, SP-1000 on Carbosphere packing.

Elution of Chlorocarbons from samples with a Purge-Trap Apparatus: Mixtures of vinyl chloride and other chlorocarbons were injected, collected, and purged from the apparatus and % recovery determined over several purging cycles. The recovery of these materials was less than 100% on a single pass. More details on this experiment are given in the Results section. Systems were calibrated using pure water. Chlorocarbon recovery from samples including sewage or landfill material was much less due to adsorption on solid material.

Head-Space Analysis of PVC, Saran, and Polyethylene for Residual VC Monomer: Samples of PVC, Saran, and polyethylene were obtained from existing laboratory supplies. The amounts of residual VC monomer were determined by an indirect headspace method. The PVC pipe was ground to a fine powder before headspace analysis. One sample was >10 years old and the second sample was estimated at <1 year old. The Saran wrap and polyethylene garbage bag were used as-received. The procedure involved placing 1.0 g of material in a septum-capped vial, heating the vial to 110°C for 1 hr, then removing the headspace gas by means of a gas-tight syringe. The headspace gases were analyzed by GC using both PI and FI detectors and by GC/MS. The detection limit for residual VC monomer was 0.2 μg/g of polymer.

Pyrolysis Apparatus: This consisted of a 0.5 x 6 in pyrex pyrolysis tube heated by a tube furnace. A sample of landfill material (~ 20 g) was placed in the apparatus, which was then flushed with argon at a flow rate of 1 ml/min. The sample was heated to 650°C over 45 min. Additional experiments were performed with landfill material mixed with PVC powder. Pure PVC without landfill material were also pyrolyzed. Gas samples were collected in a gas manometer trap, and were then analyzed by GC/MS for organic compounds, and by GC for major gas components.

Photolysis Apparatus: The apparatus used for photolysis consisted of a 15 ml quartz cell containing ~ 5 g of test material. The test material consisted of landfill surface cover to which 10 μl of labeled TCE was added. The cell was flushed with argon for the inert gas photolysis experiment. Normal air was used for the landfill surface simulation experiment. Each matrix was irradiated by a 450 W Hanovia UV lamp for 2 hr. (These conditions are known from the literature to be sufficient to cause TCE photolysis and are considerably more intense than normal California surface sunlight over a 1-day period.) Inclusion of the surface soil was necessary to test for any photocatalytic effects.

Irradiation of Landfill Materials: Gamma irradiation is a way of cold-sterilizing landfill material. Autoclaving in steam is the standard approach which was also used, but this has the disadvantage that at the autoclaving conditions (121°C for 30 min at 15 psig) chemical changes can occur which could conceivably lead to the hydrolytic formation of vinyl chloride. Gamma irradiation was performed on a total of 16 samples, which each received 2.5 megarad from a cobalt-60 source. The samples so treated were then incubated with ^{13}C-TCE to determine if there was any degradative activity. Inorganic analysis was performed by the Inductively Coupled Plasma (ICP) technique described in Appendix C.

Chlorocarbon Hydrolysis Experiment

Sterilized blank samples were prepared to determine if the test chlorocarbons can react directly with water to produce vinyl chloride. The compounds tested were 1,1-dichloroethylene, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, and 1,1,2,2-tetrachloroethane. Deionized water and sample vials were sterilized in an autoclave, substrates inoculated into the vials, and the vials incubated inside a dark growth chamber at 35°C. Individual samples were removed periodically and analyzed by the purge-trap technique to determine the degree of hydrolysis under incubation conditions.

Incubation of Sewage Sludge With Chlorocarbon Substrates

A set of 48 vials was inoculated with 30 ml of sewage sludge diluted 10:1 with deionized, organic-free water and 10 µl of chlorocarbon in methanol with methanol as a carbon source for bacterial metabolism. The source of the sewage sludge was the #2 anaerobic digester at the Richland Wastewater Treatment Plant. Sample identification and the chlorocarbon added to each vial are listed in Table 9. Care was taken in this experiment to exclude all oxygen from the test vials. Controls consisted of water and methanol only (no chlorocarbon or sludge). Duplicate vials were sampled by the purge-trap technique after 1, 3, 6, and 10 weeks of incubation at 35°C.

The sample and experiment identification system used throughout this work is explained as follows: Experiments were designated according to the microorganism source (Richland, R), date of initial inoculation (1-20 = 1-20-86), an abbreviation for the chlorocarbon (for example, VC = vinyl chloride), and further abbreviations for water- and methanol- only controls. This system was followed throughout the project for QA purposes and for ease of sample identification. (Blanks were designated B).

A second set of screening experiments was performed (designated as R-2-26-**) (Table 10).

Table 9: Anaerobic Sewage Sludge/Chlorocarbon Incubation Experiment

Vial #	Substrate Chlorocarbon	Designation
1-8	1,1-Dichloroethylene	R-1-20-VI
9-16	Cis-1,2-Dichloroethylene	R-1-20-CD
17-24	Trans-1,2-Dichloroethylene	R-1-20-TD
25-32	Trichloroethylene	R-1-20-TR
33-40	1,1,2,2-Tetrachloroethane	R-1-20-PE
41-48	Vinyl Chloride	R-1-20-VC
49-56	Water blanks	R-1-20-BW
57-64	Methanol blanks	R-1-20-BMe

R = Richland sewage sludge inoculum; 1 = Month #1; 20 = Day inoculated (1-20-86); last two symbols indicate chlorocarbon added (list below), or whether water (BW) or methanol (BMe) was added to the vial as a control blank.

Chlorocarbon abbreviation list: VC = Vinyl Chloride; CD = Cis-1,2-dichloroethylene; TD = Trans-1,2-dichloroethylene; VI = Vinylidene chloride (1,1-Dichloroethylene); TR = Trichloroethylene PC = Perchloroethylene (Tetrachloroethylene); DE = 1,1-Dichloroethane; DC = 1,2-Dichloroethane; MC = 1,1,1-trichloroethane; TE = 1,1,2-Trichloroethane; PE = 1,1,2,2-Tetrachloroethane.

Table 10: Sewage Sludge/Chlorocarbon Incubation Without Oxygen Exclusion.

Vial #	Substrate Chlorocarbon	Designation
1-8	Vinyl Chloride	R-2-26-VC
9-16	1,1-Dichloroethane	R-2-26-DE
17-24	1,2-Dichloroethane	R-2-26-DC
25-32	1,1,1-Trichloroethane	R-2-26-MC
33-40	1,1,2-Trichloroethane	R-2-26-TE
41-48	Lab. TCE	R-2-26-13C*
49-56	Tetrachloroethylene	R-2-26-PC
57-64	Water blanks	R-3-12-BW
65-72	Methanol blanks	R-3-12-BMe

* Lab. TCE refers to ^{13}C-labeled TCE in this experiment. Vinyl chloride was added from a stock solution made by bubbling 100 ppm vinyl chloride in nitrogen into methanol at -196^{o}C and determining the VC concentration by GC.

The samples were prepared in the same manner as the first experiment. A fresh sample of waste water from the anaerobic digester at the City of Richland sewage treatment plant was obtained for inoculation of the test vials. The chlorocarbons used in these samples were 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, tetrachloroethylene, and ^{13}C-labeled TCE. Separate samples were inoculated with methanol (control) and vinyl chloride, to determine their rates of degradation under these conditions. The results from these screening experiments were not as reproducible as expected, so another sample preparation procedure was employed.

The sample preparation procedure employed sewage sludge diluted 5:1 with deionized water and no attempt was made to initially exclude oxygen from the vials. The vials were incubated for one week in which time the bacteria present had removed all the oxygen from the vials. They were then injected with the chlorocarbon diluted in methanol through the septa, inverted, and placed back into the growth chamber. Twenty-four vials (designated as R-3-4-**) were prepared by this procedure, 10 each with 1,1,1-trichloroethane and 1,1-dichloroethene spikes and 4 left as unspiked blanks. This sample preparation procedure resulted in much better reproducibility and was used for all subsequent sample preparation.

Optimum incubation temperature was determined by incubating 110 sample vials at 35 or 55^{o}C. For growth at 35^{o}C, 44 samples were prepared (R-4-4-** -35) with 12 ^{13}-C-TCE spiked, and 8 each with <u>cis</u>-1,2-dichloroethylene, <u>trans</u>-1,2-dichloroethylene, VC, and water blanks. For growth at 55^{o}C, 40 samples were prepared (R-4-4-**-55) with 10 each of 1,1-dichloroethylene, TCE, and VC spikes, and 8 each of ^{13}C-TCE-spiked, and methanol blanks. Another 20 vials were prepared using material from a 1 liter anaerobic reactor held at 55^{o}C for 2 months and with methanol as carbon source. The vials (A-4-4-**) were spiked 4 each with 1,1-dichloroethylene, ^{13}C-TCE, <u>cis</u>-1,2-dichloroethylene, <u>trans</u>-1,2-dichloroethylene, and 4 water blanks. These vials were placed in a growth chamber with the other vials incubated at 55^{o}C.

Blanks (B-3-12-**) were prepared using sterilized water spiked with 1,1-dichloroethylene, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, and 1,1,2,2-tetrachloroethane. The samples were incubated at $35^{0}C$ for up to 6 months.

In a further control experiment, a series of vials containing sewage sludge was autoclaved twice (1 day apart) and incubated for 2 months after inoculation with 10.0 μl methanol and 10 μl of labeled TCE or unlabeled 1,1,1-trichloroethane dissolved in methanol. Incubation was at 35 and $55^{0}C$ for one-half of each subset.

Incubation of Landfill Material With Chlorocarbon Substrates.

Sample Receipt, Storage, and Vial Preparation: Upon receipt at Battelle, the landfill samples were immediately examined to make sure that they were undamaged and not exposed to air. They were then transferred to an anaerobic glove bag filled with 50% argon and 50% carbon dioxide. The headspace oxygen content and physical appearance of the samples in the individual sample bags were determined and recorded. (Oxygen content was determined using a Carle Series 400 GC system, by injection of 0.7 ml of headspace gas.) Gas samples were removed by syringe directly from the samples, for headspace analysis for chlorocarbons and other organic volatiles. Portions of the landfill material were removed from each sample and checked for visual homogeneity. (Highly unrepresentative samples containing large rocks or samples containing only one material such as paper were returned to their respective bags and more representative material taken). The appropriate amount of landfill material was then placed in a labeled vial (from which air had previously been flushed out by the inert gas mixture in the glove bag) and the vial was capped and sealed before being removed from the glove bag. Sample weights and original sources for each vial were noted. These samples were used for pyrolysis, photolysis, irradiation, and incubation experiments as noted in the Tables below. Unused landfill materials were stored in their original containers at $20^{0}C$ in a dark room in case additional samples were needed.

Landfill Material Incubation Experiments: About 10 g of each landfill sample was taken from the bulk core material in an atmosphere of 50% argon/50% carbon dioxide in a glove bag as described above, weighed, and used directly.

The assay system for determining chlorocarbon conversion is similar to that described above for sewage incubation experiments and is based on the methodology of Parsons et.al. (1984). Reaction vials containing the landfill sample and having a capacity of 40 ml were filled to 30 ml with sterilized water in a glove bag containing a mixture of 50% argon:50% carbon dioxide. The vials were removed from the glove bag and placed in a growth chamber held at 35°C. The chlorocarbon substrates, dissolved in methanol, were added by syringe through the septa after 1 week of incubation. The reaction vials were incubated without agitation at a temperature of 35°C). Incubations were terminated after 1, 3, 6, and 10 weeks. Each sample was prepared in duplicate. The solvent (methanol) was HPLC grade to avoid problems with contaminants. The vial caps have an opening in them and a teflon/silicone septum (to eliminate extraction of plasticizers - phthalates - into the vial liquid contents). At the termination of the incubation period the chlorocarbon substrates and products were analyzed by the purge-trap technique. Tables 11 and 12 provide information on the microcosm compositions in vials used for incubation of landfill samples from Sites A and B (Not all samples incubated were analyzed, for reasons of time and economy and to avoid redundant data. The most active samples were determined by the amount of gas production).

Table 11: Landfill Site A Incubation Experiments

Sample/Vial #	Vial Content	Sample/Vial #	Vial Content
A-1-S-1 to 6	Blanks (BW, BMe)	A-1-3-1 to 6	Blanks (BW, BMe)
A-1-S-7 to 12	Not done	A-1-3-7 to 10	VI
A-1-S-13 to 15	ICP Analysis	A-1-3-11 to 14	TCE
A-1-S-16 to 17	Pyrolysis	A-1-3-15 to 22	Lab. TCE
A-1-S-18 to 19	Photolysis	A-1-3-23 to 25	ICP Analysis
A-1-S-20 to 22	Headspace gas	A-1-3-26 to 27	Pyrolysis
A-1-S-23 to 24	60-Co steril'n.	A-1-3-28 to 29	Photolysis
		A-1-3-30-to 32	Headspace gas
A-2-S-1 to 24	As above.	A-1-3-33 to 34	60-Co steril'n.
		A-1-10-1 to 34	As above.
		A-2-6-1 to 34	As above.
		A-2-16-1 to 34	As above.

S = Surface cover sample; A-1-, A-2- refer to core #1 and #2, respectively; A-1-3-** = 3 ft. depth sample; A-1-6-** = 6 ft; A-2-16-** = 16 ft depth.
Lab. TCE = labeled TCE.

Table 12: Landfill Site B Incubation Experiments

Sample/Vial #	Vial Content	Sample/Vial #	Vial Content
B-1-S-1 to 6	Blanks (BW, BMe)	B-1-4-1 to 6	Blanks (BW, BMe)
B-1-S-7 to 12	Not done	B-1-4-7 to 10	VI
B-1-S-13 to 15	ICP Analysis	B-1-4-11 to 14	TE
B-1-S-16 to 17	Pyrolysis	B-1-4-15 to 22	lab. TCE
B-1-S-18 to 19	Photolysis	B-1-4-23 to 25	ICP Analysis
B-1-S-20 to 22	Headspace gas	B-1-4-26 to 27	Pyrolysis
B-1-S-23 to 24	60-Co steril'n.	B-1-4-28 to 29	Photolysis
		B-1-4-30-to 32	Headspace gas
B-2-S-1 to 24	As above.	B-1-4-33 to 34	60-Co steril'n.
		B-1-10-1 to 34	As above.
		B-2-3-1 to 34	As above.
		B-2-10-1 to 34	As above.

S = Surface cover sample; B-1-, B-2- refer to core #1 and #2, respectively; B-1-4-** = 4 ft. depth sample; B-1-10-** = 10 ft; B-2-3-** = 3 ft depth. Lab. TCE = labeled TCE. TE = 1,1,1-Trichloroethane.

Incubation of Landfill Material with Labeled Trichloroethylene:

An important experiment was designed to show that vinyl chloride is in fact produced from the added chloroethylenes and does not accumulate from an endogenous pool within the core sample. To demonstrate that exogenously supplied chloroethylenes are converted to vinyl chloride, carbon-13 labeled TCE was incubated with reaction mixtures derived from core sample material in water. Carbon isotope ratios of all chloroethylene products including vinyl chloride were determined by GC/MS. An accumulation of carbon-13 enriched products would demonstrate that the biological reaction is occurring in the landfill core samples. There was no plan to use other labeled precursors (e.g., dichloroethylenes) if the labeled TCE led to the formation of labeled dichloroethylenes and labeled vinyl chloride, since this experiment would have conclusively established the interconversion between these materials. An additional factor in this decision was the very high cost of labeled dichloroethylenes. The experiment consisted of 8 vials inoculated with material from each landfill site sample.

Isolation Experiments for Vinyl Chloride-Producing Organisms:

Preliminary experiments showed that the biological formation of vinyl chloride was relatively slow. To boost this rate it was necessary to have a large population of easily accessible microorganisms. Standard microbiological methods were not useful in this regard. Instead of isolating and selecting single colonies on agar medium, we used a 2 liter anaerobic fermentor, which provided the necessary quantities of culture. For assay, a sample vial could be filled directly from the fermentor jar by means of a sampling device, with minimal exposure to air. The growth medium used consisted of the basal salts medium described for the roll-tube method (below) supplemented with 1 ml/l of HPLC grade methanol. Gases produced in this fermentor were collected by water displacement in a liquid-filled gas meter with graduated markings. After consumption of each batch of added methanol, more methanol (1 ml/l) was added, approximately once per day. After sample removal from the fermentor, fresh deoxygenated liquid medium was used to make-up the volume. Deoxygenation was achieved by argon-sparging for 30 min. Culture samples were plated on agar either on Petri dishes in a GasPak anaerobic jar or by the Hungate roll-tube method.

The anaerobic system used for strict anaerobes (the roll-tube method) was described by Hungate (1969). The medium used consists of mineral salts supplemented with 1 ml/l of HPLC grade methanol. The mineral salts added to the medium are as follows:

Disodium hydrogen phosphate	9 mM;	Potassium dihydrogen phosphate	9 mM
Ammonium sulfate	15 mM;	Magnesium sulfate	2 mM
Sodium chloride	0.1 mM;		
Calcium chloride	20 µM;	Cobalt chloride	5 µM
Copper sulfate	1 µM;	Ferrous sulfate	1 µM
Manganous sulfate	1 µM	Sodium molybdate	4 µM
Zinc sulfate	0.5 µM;		

Each tube contained 5 ml of medium supplemented with 2% agar (Difco). Cysteine (0.03%) and hydrogen sulfide (0.125 ml) per tube were added to the tubes after inoculation, as additional reductants. Also, 0.0001% reasurin was added to the cultures as a redox indicator. The tubes were purged with a gas mixture containing 50% argon and 50% carbon dioxide, and incubated at 35°C.

Conclusion:

These experiments were designed to provide the maximum information on the cause(s) of vinyl chloride emissions from landfills in California. The experimental plan was designed to provide the flexibility needed to respond to unexpected situations and to information derived at earlier stages in the experimental work. The next section describes the results obtained in practice.

EXPERIMENTAL RESULTS

Our experience in obtaining landfill samples and the results of experiments to determine the source of vinyl chloride emissions from landfills are presented here. The order of presentation is not always the same as the order in which the experiments were performed. Instead it represents a logical sequence from pure materials treated with a single agent through complex and contaminated landfill materials which may have been exposed to a wide range of different conditions leading to vinyl chloride formation. The description of experimental results is concluded with microbial isolation experiments which once again deal with defined systems.

LANDFILL SAMPLING RESULTS

Site A:

The refuse removed from the 2 boreholes A1 and A2 included common household refuse components such as plastic, paper, cloth, etc. The organic refuse material removed from borehole A1 was relatively dry and was uniformly brown. The organic material removed from borehole A2 was similar to that from A1 to a depth of ~ 8 ft. Below that, the refuse became darker, with apparently more moisture.

The unsatisfactory cover at sampling location A2 caused difficulty in sample collection. On the first drilling attempt, excessive cobbles in the cover material prevented penetration of the cover. On the second drilling attempt the refuse cover depth was found to exceed 10 ft; samples could not be taken at the 10 ft refuse depth (i.e., 20 ft total depth) with the equipment on-site. The boring location was therefore moved ~ 100 ft and the sampling was successfully achieved.

Removing sample A2 at 4 ft was also difficult. Several attempts were needed to remove sufficient sample, and hence the total sample contained material from the 4-6 ft refuse depth. To provide refuse and gas samples and gas samples from sampling points separated vertically by a minimum of 5 ft, and to sample the refuse in the lower, more moist refuse below 8 ft, this borehole was extended to a refuse depth of 16 ft before a second sample was collected.

Samples of refuse and gas were forwarded to Battelle-Northwest by Federal Express on May 7, 1986, and were received at the laboratory on the morning of May 8.

Site B:

At Site B, the refuse removed from the boreholes included common household refuse components such as plastic, paper, and cloth. The organic refuse material removed from both boreholes was relatively dry. No undue difficulties were encountered in obtaining the samples from Site B. The samples were forwarded to Battelle-Northwest on May 19, 1986, and received the following morning.

SAMPLE DESCRIPTIONS AND ON-SITE MEASUREMENTS:

On-site measurements recorded at both sites are presented in Table 13. Additional gas sample analysis was performed on receipt at Battelle to determine if any leakage of air into the samples had occurred.

Oxygen levels in the gas from buried samples was at or less than the 1.2% background normally experienced. This indicates that problems encountered in getting the samples from the sampling tube into the bags should not have significantly raised the oxygen stress on the organisms. The samples spent 2 nights at or below $20^{o}C$, plus one day in an airplane, and the effect of this on viability was unknown at the time.

Individual Sample Descriptions:

As commented earlier, there is no such thing as a "representative" landfill sample. However, the following visually determined observations on sample appearance are useful in determining the nature of the original material in the sample, and the approximate degree of decomposition.

Table 13: Site A and B Refuse and Gas Sampling Conditions.

Sample ID #	Description	Refuse Interval	Temp. (°F)	pH	Methane (%)	Oxygen (%)
A-1-S	Surface cover	-0-	78	NR*	-0-	21+
A-1-3	Refuse + Gas	3-4	78	5.6	62	-0-
A-1-10	Refuse + Gas	10-11	78	6.4	62	-0-
A-2-S	Surface cover	-0-	88	NR	-0-	21
A-2-4	Refuse + Gas	4-8	91	6.2	55	-0-
A-2-16	Refuse + Gas	16-18	90	6.1	51	T#
B-1-S	Surface cover	-0-	88	NR	-0-	21
B-1-3	Refuse + Gas	3-4	88	5.4	50	-0-
B-1-10	Refuse + Gas	10-11	96	7.0	54	-0-
B-2-S	Surface cover	-0-	98	NR	-0-	21
B-2-3	Refuse + Gas	4-6	98	5.2	50	-0-
B-2-10	Refuse + Gas	10-11	119	4.9	50	-0-

All depths in feet; soil cover depth at both locations was ~ 2 ft. Ambient temperature was 68°F. Refuse Interval refers to depth below cover base.
* NR = Not Recorded; + = +/- 1%; # = Trace, <1%.
Measurement precision: Refuse interval, +/- 0.25 ft; Temperature +/- 0.5°F; pH +/- 0.05 pH units; methane and oxygen concentrations +/- 1%.

Cover samples A-1-S and A-2-S consisted of yellow, coarse-grained sand and rocks, as expected. The largest rocks in the received samples were about 1-2 cm in diameter. The cover samples from Site B consisted of black dirt with some small gravel.

At the intermediate depth at Site A, the sample at location #1 (A-1-3-) contained much paper with print still readable (i.e., little decayed), while at location #2 (A-2-6-) there was some paper, foam, some rocks, and metal. Site B intermediate samples at location #1 (B-1-3-) contained sandy soil, paper, and plastic wrapping, and at the second location (B-2-3-) contained grass clippings in addition to these materials.

At the greatest depths sampled, considerable refuse decay had occurred in all samples. At Site A (A-1-10-) there was decayed material resembling tree bark, plus dirt, rocks, and unrecognizable material. Sample A-2-16- also contained some decaying wood. Site B (B-1-10- and B-2-10- samples) contained decayed grass clippings, plastic wrapping, metal foil, decayed cloth, and unidentifiable metal objects. The Site B samples appeared to be much wetter than the Site A samples at this depth.

The original intent in obtaining samples at two depths was to obtain material at the beginning, and well into, the anaerobic zone. From the appearances of these samples, this objective was achieved.

VINYL CHLORIDE FORMATION BY CHEMICAL ROUTES

Hydrolysis of Chlorocarbons:

Although not specifically investigated, one observation is of interest. Autoclaved vials to which 1,1,2-trichloroethane had been added after sterilization yielded 1,1-dichloroethylene as a product, in the absence of any detectable microbial growth. This result indicates that a non-biological conversion of chloroeth<u>a</u>nes is possible, leading to the formation of biodegradable chloroethylenes. Of course, this does not exclude the concurrent existence of a biological route between these two compounds.

Pyrolysis Experiments:

Because of its chemical nature, vinyl chloride polymer (polyvinyl chloride, PVC) must initially be a prime suspect as a source of vinyl chloride emissions. If not the polymer itself, then perhaps the wastes from PVC production (PVC waste sludges), which contain large amounts of unreacted monomer. Information available from the literature, however, strongly indicates that PVC cannot be a source of significant amounts of vinyl chloride. The operators of sites A and B informed us that PVC waste sludges were never allowed to be dumped in either landfill. When landfill samples were visually inspected, only small pieces of plastic were noted, including some garbage bag material. Saran is a PVC-type material crosslinked with vinylidene chloride (1,1-dichloroethylene). In principle, depolymerization reactions could lead to vinyl chloride formation, but in practice, the decomposition takes place by a completely different mechanism leading to benzene as the principal product. One remaining possibility was that "old" samples of PVC

(>10 years) could contain larger amounts of residual monomer, since at the time of manufacture vinyl chloride was not recognized as hazardous. For this reason, and to confirm that PVC does not yield vinyl chloride, we performed pyrolysis experiments. Also, in case landfill material could exert some catalytic effect which might alter the PVC decomposition mechanism with the formation of vinyl chloride, we included landfill material/PVC mixtures in the experiments. The following results were obtained:

Head space analyses were performed on PVC pipe, Saran wrap, and garbage bag material (mostly polyethylene). The sample containing the most residual vinyl chloride monomer was an 8-10 year old threaded PVC fitting (containing 336 μg/g). A 1-year old PVC pipe sample contained only 3 μg/g of residual vinyl chloride monomer. Neither fresh Saran wrap nor garbage bag material contained detectable levels of vinyl chloride by head space analysis.

PVC, landfill material, and landfill material plus PVC were pyrolyzed to 650°C. Gas samples were collected for analysis at 150, 350, 500, and 650°C. PVC (2 g) began decomposing at 150°C. Vinyl chloride was detected in all gas samples up to 650°C. Yields of vinyl chloride were no greater than expected from residual monomer content.

Landfill material (20 g) from A-2-16 was pyrolyzed. No vinyl chloride was detected in any of the gas samples. Fixed gas analysis showed the decomposition gas to consist of hydrogen (54%), carbon dioxide (31%), carbon monoxide (5.6%), and methane (9.2%). After pyrolysis, 13.8 g of char remained.

Landfill material (18 g) from A-2-16 was mixed with PVC (2 g) and pyrolyzed to 650°C. Gas samples at all temperatures contained vinyl chloride at concentrations similar to those from the PVC-only pyrolysis experiment. The product gas contained hydrogen (44%), carbon dioxide (22%), ethylene (1.5%), ethane (4.7%), methane (21%), and carbon monoxide (6.1%). The formation of hydrogen chloride from PVC pyrolysis greatly increased the production of condensable liquid from landfill material. After pyrolysis, 13.5 g of char remained.

Photolysis Experiments:

Formation of vinyl chloride by photolysis of precursors in air is a possible mechanism which has been discussed previously, and found to be unlikely. Loss of chlorine radicals from TCE would be expected to produce chloroacetylene; in the presence of oxygen from air, chloroacetaldehyde is formed. Photolysis of PVC itself is known to lead to similar decomposition products to those formed during pyrolysis. However, in the presence of landfill cover material, there exists the possibility that a photo-assisted catalyzed reaction could take place. Similar syntheses are known (e.g., formation of formic acid from CO and water over silica). The landfill cover is primarily sand and clay, both in theory capable of modifying the normal photolysis reaction sequence. Experiments were performed to check this hypothesis, as follows:

Surface soil samples from the landfill sites were photolyzed in the presence of ^{13}C-labeled trichloroethylene. Soil (5 g) was placed in a 5 ml quartz cell, spiked with the labeled TCE, and then photolyzed for 2 hr in air and in argon with a 450 watt Ace-Hanovia UV lamp source. Photolysis in air resulted in formation of labeled chloroethyne (chloroacetylene). In argon, the only compound detected was unlabeled benzene. This probably arose from photolysis of toluene, which was one of the major organic contaminants found in the landfill samples.

Effect of Steam and Gamma-Irradiation Sterilization:

Autoclaving and irradiation were used to kill any viable microorganisms in the samples, with the intent of showing that any vinyl chloride-producing activity ceased after treatment. This would strongly implicate viable microorganisms as the causative agents of vinyl chloride formation from materials pre-existing in the landfill. Autoclaving was for 15 min at 121^{o}C, the standard conditions for routine sterilization. A total of 16 samples were irradiated with cobalt-60 gamma rays to a total dose of 2.5 megarad. The sample vials were filled with sterilized water. Half were spiked with methanol only, and the other half with methanol plus ^{13}C-trichloroethylene. Biological activity was monitored by headspace gas analysis, and vinyl chloride production by the normal purge-trap method. Disappearance of oxygen and the appearance of H_2, CO, CO_2, and CH_4 was used to indicate the presence of biological activity. (Radiation sterilization was not always fully effective, even at 2.5 MR.) Absence of vinyl chloride formation together with a lack of biological activity would have indicated that vinyl chloride formation is associated with viable microorganisms in the landfill samples. No vinyl chloride was detected from autoclaved sewage sludge samples after 5 weeks incubation. In no case did an autoclaved landfill sample that showed no biological activity also produce vinyl chloride. The autoclaving was only successful in sterilizing ~ 20% of the samples (a very low proportion, either demonstrating the ability of anaerobes to withstand heat or that they were protected in some way by the aggregate landfill material). Irradiation sterilization was successful in ~ 50% of the samples, and again, no vinyl chloride was produced from any vial that did not show biological activity. The association between the existence of viable microorganisms and production of vinyl chloride from labeled TCE is therefore shown by these experiments.

CHEMICAL ANALYSIS OF LANDFILL MATERIAL

A knowledge of the composition of the landfill material is essential in order to postulate vinyl chloride formation mechanisms. The presence or absence of a particular material in a given sample (e.g., TCE) coupled with the presence or absence of vinyl chloride constitutes good circumstantial evidence for or against specific formation mechanisms. For this reason, we performed detailed organic and inorganic analyses of our landfill samples. However, with so few samples taken from such heterogeneous mixtures, we do not claim that the following compositions are in any sense "normal" or "average". We also determined the head-space gas composition above the samples, to obtain an indication of the nature of any volatile organic compounds present and to determine whether or not there was active anaerobic digestion still occurring. Because of the large amount of laboratory work involved, not all measurements were made on all samples. The following information was obtained:

Volatile and Ash Analysis:

Volatiles (primarily water) and ash determinations have been made for six of the landfill samples, including surface soil. Volatiles were determined by heating the samples at 110^{o}C under vacuum, and therefore include organic solvents as well as water. Ash contents were determined on the dry samples from volatile analysis, by heating at 750^{o}C for 8 hr. The samples were extremely inhomogeneous, as expected for the type of material, so these analytical data should be considered indicative rather than representative. The results are presented in Table 14:

Table 14: Volatile and Ash Contents of Landfill Samples

Sample ID	Sample weight	Moisture* Wt.	Moisture* Wt.%	Sample Dry wt.	Final wt.+	% Residue (ash)
A-1-1-25	7.5425	2.6881	35.64	4.8544	3.0335	62.5
A-1-S-14	10.4442	1.1022	10.55	9.3420	8.9955	96.3
A-2-16-28	15.2425	3.0351	19.91	12.2074	10.9635	89.8
B-1-3-27	11.7681	1.4983	12.73	10.2698	9.4839	92.4
B-2-S-16	19.0348	2.9061	15.27	16.1287	15.2232	94.4
B-2-10-27	3.4187	0.8923	26.10	2.5264	1.3479	53.4

* Moisture - includes volatile organics;
\+ Difference between sample weight and moisture weight = sample dry weight.
Sample ID Sequence is: Location (Site A or Site B); Bore #; Depth (S = cover); Sample reference # (1-34).

Inorganic component analysis of landfill material was performed by the ICP (Inductively Coupled Plasma) technique (Appendix `C'), with results as shown in Table 15. Detection limits in Table 15 are given in μg/ml. Elements not listed were either not detected or are not detectable by ICP. A hyphen in Table 15 indicates that the element, if present, was below the detection limit. Sample labeling is the same as that used in previous reports of sample #. For example, B-2-S-16 = Site B, second core, Surface sample, tube #16.

Gas sample analyses were also performed. Data for the location containing the highest amount of vinyl chloride (A-2-16) is shown in Table 16, below. Figure 9 shows the total ion monitor traces from 33 to 200 amu for landfill gas samples, determined by head-space analysis. The presence of vinyl chloride was confirmed by the presence of a peak at m/e 62.

Table 15: ICP Inorganic Component Analysis of Landfill Samples

Element	Detn.*	Sample #					
(Wt.%)	Limit	B-2-S-16	B-1-3-27	B-2-10-27	A-1-S-14	A-1-1-25	A-2-16-28
Al	0.03	6.45	7.80	6.33	6.71	7.29	6.23
B	0.01	0.04	0.04	0.04	0.04	0.08	-
Ba	0.002	0.06	0.07	0.06	0.13	0.10	0.10
Ca	0.01	1.39	1.60	3.07	0.64	3.80	1.86
Cu	0.004	0.01	-	-	0.02	0.03	0.03
Fe	0.005	3.78	4.03	3.29	3.38	4.04	4.88
K	0.3	1.43	1.55	0.99	2.36	2.22	1.87
Li	0.004	0.02	-	0.02	0.03	-	0.02
Mg	0.06	1.21	1.21	1.07	0.62	1.00	0.83
Mn	0.002	0.07	0.08	0.07	0.07	0.09	0.09
Na	0.01	1.21	1.49	2.10	1.68	1.40	1.48
Si	0.02	31.9	30.8	31.0	32.6	28.5	31.5
Sr	0.002	0.02	0.04	0.03	0.02	0.02	0.02
Ti	0.002	0.39	0.30	0.40	0.24	0.57	0.25
Zn	0.02	-	-	0.04	-	0.09	-
Zr	0.008	0.05	0.02	0.05	0.04	0.05	0.02

Head space gas analyses were performed by heating the samples in a septum-capped vial for 1 hr at 110^{o}C. Gas samples of 1 or 5 ml were then directly removed by syringe through the septum and injected into the GC/MS. Head-space analyses of samples should be considered as qualitative only, as volatile components would have been lost during field handling. However, after sealing samples in plastic, head space gas analyses were useful indicators of organic compounds present in samples and of ongoing biological activity. Chlorinated ethylenes and ethanes were present in the Site A landfill head-space samples, but none in the Site B gas samples. Also, dichloromethane was present in the Site A but not in the Site B samples. Many of the compounds identified by head-space analysis of the Site B samples can be attributed to

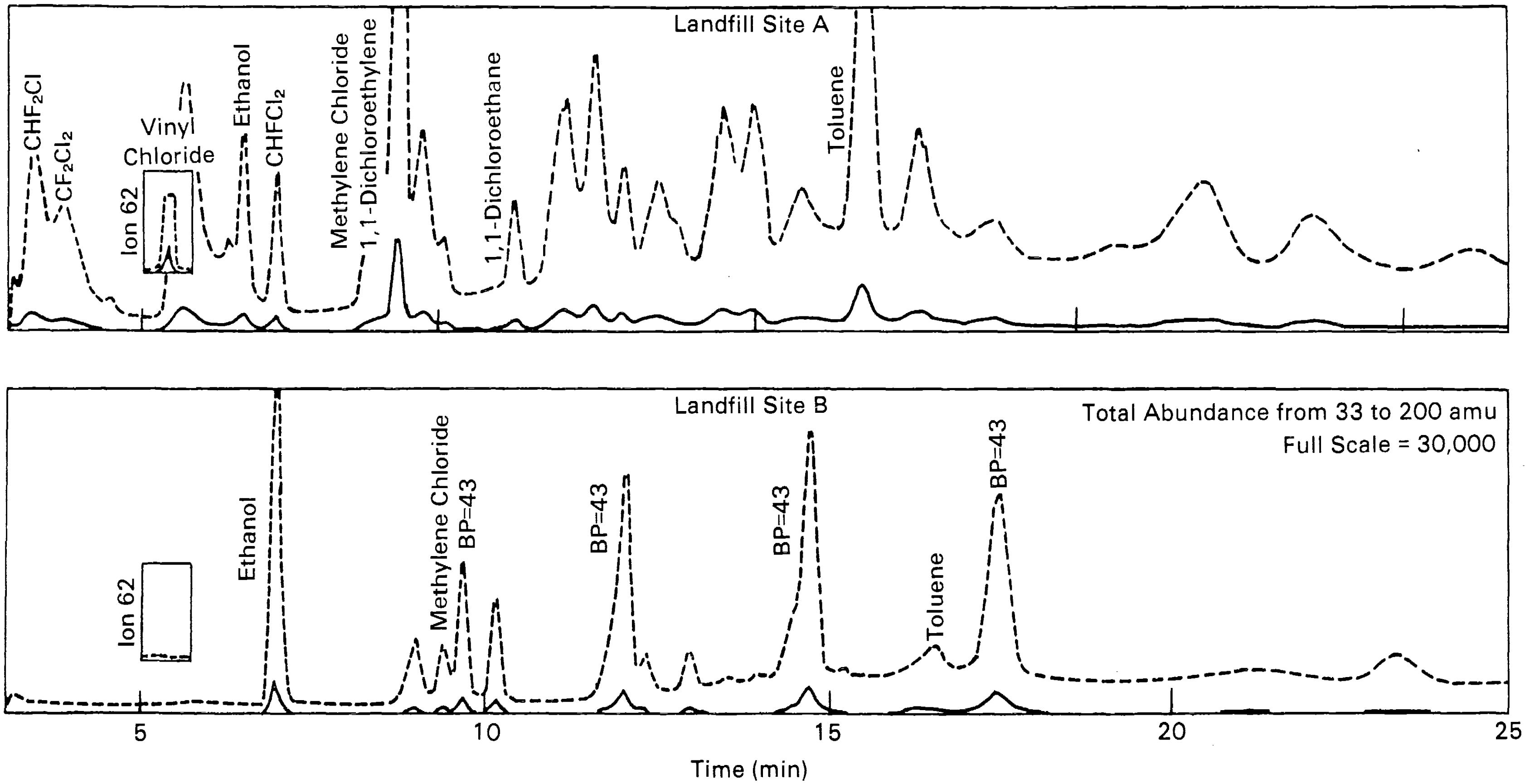


FIGURE 9. Total Ion Monitor (GC/MS) Trace for Gas Samples from Landfill Sampling Sites

a biological origin, such as acetone, ethanol, propanol, acetaldehyde, methanethiol (methyl mercaptan), and carbon disulfide. Others such as propene are unlikely to be produced biologically, and we have seen no reports suggesting biological formation of this compound. Site B samples contained low levels of toluene, a very common solvent which was present in large amounts in the Site A samples. Toluene concentration is a good indicator of the different characters of the two sites - Site A has accepted solvents in the past, while Site B has taken relatively little solvent-containing material, mostly of household origin. Vinyl chloride was not found by head space analysis of any sample from either site probably because of its volatility and loss during sample packing, although vinyl chloride was found in the gas samples taken at Site A. Data obtained from three of these samples is shown in

Table 16: Trace Organic Component Analysis of Gas Sample A-2-16

Peak #	Retention (min.)	Identity	Rel. peak size*
1	3.12	Chlorodifluoromethane	1
2	3.44	Propene (propylene)	2
3	5.1	Dichlorodifluoromethane	2
4	5.8	Chloroethylene (VINYL CHLORIDE)	5.14+/-0.1 ppm
5	5.8	Isobutane	3
6	6.7	Unknown	1
7	7.0	Ethanal (acetaldehyde)	3
8	7.5	Dichlorofluoromethane	2
9	9.3	1,1-Dichloeoethylene	Trace
10	9.3	Dichloromethane	4
11	9.8	_n_-Pentane	2
12	10.1	Unknown	1
13	11.1	_cis_-Dichloroethylene	Trace
14	11.2	1,1-Dichloroethane	1
15	11.9	Unknown	2
16	12.5	Unknown	2
17	12.7	Unknown	1
18	13.3	1-Hexene or cyclohexane	2
19	14.4	Unknown	2
20	14.8	Unknown	2
21	16.4	Toluene	4
22	17.6	Unknown	2
23	20.1	_m_- or _p_-Xylene or Ethylbenzene	3
24	23.9	Unknown	2

* 1 = 1 ppm or less; 3 = 1000 ppm or less; 4 = more than 1000 ppm.

Table 17. (Note that the amounts are given in relative peak heights which should not be equated to actual quantities because of differing detector responses for different classes of organic compound and because of baseline spreading with increasing retention time.)

Table 17: Head Space Gas Analyses From Site A and B Samples

Compound	Rel. Peak Ht.*	Retention (min).
Site A (Sample A-2-16-31)		
Acetaldehyde	14.7%	5.44
Methanethiol	1.5	6.18
Ethanol	26.1	7.12
Dichlorofluoroethane	3.6	7.44
Acetone	16.8	8.88
Dichloromethane	100	9.32
1,1-Dichloroethylene	Trace	9.32
cis-1,2-Dichloroethylene	2.7	11.44
Methyl ethyl ketone (MEK)	14.6	11.62
Ethyl acetate	14.0	11.94
Unknown	2.1	12.26
1,2-Dichloroethane	1.4	12.76
1-Butanol	16.5	12.94
Trichloroethylene (+ unknown)	11.5	13.50
	21.6	13.56
Unknown (m/e 43 base peak)	3.3	14.00
Ethyl propanoate	9.6	14.26
Methyl butanoate	13.2	14.62
Unknown	7.8	15.44
Toluene	78.5	16.44
Ethyl butanoate	32.1	17.44
Xylene	26.8	21.62
Unknown mixture (m/e 43 base peak)	40.3	23.3
Site B (Sample B-2-3-24)		
Propene	4.8	3.32
Acetaldehyde	44.7	5.44
Methanethiol	15.6	6.26
Ethanol	10.6	7.12
Acetone	18.2	8.88
Carbon disulfide	7.0	9.76
1-Propanol	3.8	10.26
iso-Butanal (*iso*-butyraldehyde)	44.2	10.94
Methyl Ethyl Ketone (MEK)	13.8	11.62
Unknown	2.2	11.94
1-Butanol	4.3	12.94

Table 17 (Continued):

Site B (sample B-2-3-24 continued)		
Pentanal (Valeraldehyde)	100	13.50
2,5-Dimethylfuran	5.9	14.06
Methyl butanoate	1.2	14.76
Unknown	17.4	15.44
Site B (Sample B-2-10-24)		
Propene	7.3	3.38
Acetaldehyde	59.5	5.62
Methanethiol	3.2	6.50
Ethanol	19.2	7.38
Acetone	23.6	9.18
1-Propanol	10.5	10.56
iso-Butanal	50.4	11.18
Unknown	16.1	11.94
Unknown	4.2	12.26
1-Butanol	4.9	13.32
Pentanal	100	13.94
2,5-Dimethylfuran	2.5	14.56
Methyl butanoate	2.3	15.12
Unknown	21.9	15.94
Unknown	11.9	18.32
Unknown	7.2	25.06

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*Data on peak size are indicative (qualitative) only, due to loss of volatiles from samples during brief exposure to air before sealing.

VINYL CHLORIDE FORMATION BY BIOLOGICAL TRANSFORMATIONS

This section includes results obtained by the initial use of sewage sludge, which has been theoretically exposed to near-zero amounts of chlorocarbon compounds, and landfill material. Both of these types of material are very rich in multiple species of anaerobic bacteria. These bacteria have been implicated in vinyl chloride formation from TCE and other chlorocarbons.

The landfill material was obtained as described earlier. Because of the dumping histories of the two landfills, Site B should be intermediate in vinyl chloride emissions and production activity between the unexposed sewage sludge and the Site A material. Results to be given below demonstrate that this was in fact the case.

Chlorocarbon Incubation With Sewage Sludge:

Results from Experiments #1 and #2 with Richland sewage sludge are given in Table 18. These experiments were dual-purpose: To validate our experimental procedures prior to using scarce landfill material, and to determine whether vinyl chloride could be produced from other chlorocarbons by organisms which had never before been exposed to significant amounts of these materials.

Table 18: Vinyl Chloride Formation from Chlorinated Ethylenes and Ethanes.

Compound	Induction Period* (Wks.)	Amount VC (μg/total)
1,1-Dichloroethylene (Vinylidene chloride)	1	0.06
Trans-1,2-dichloroethylene	1	0.02
Cis-1,2-dichloroethylene	3	0.01
Trichloroethylene (TCE)	3	0.01
Tetrachloroethylene	6	0.00
1,1-Dichloroethane	1	0.08
1,2-Dichloroethane	3	0.01
1,1,1-Trichloroethane	3	0.04
1,1,2-Trichloroethane	1	0.48
1,1,2,2-Tetrachloroethane	6	0.03

* Time in weeks to first appearance of vinyl chloride, determined by GC/MS.

Using the second method of sample preparation, the rate of production of vinyl chloride from two selected compounds of interest - 1,1-dichloroethylene (vinylidene chloride), and 1,1,2-trichloroethane - was measured using a series of vials analyzed at 1 week intervals. The results are shown in Figure 10.

Finally, sewage sludge was incubated with labeled TCE for 1-10 weeks, and the vials subjected to purge-trap analysis of products by GC/MS analysis. A typical chromatogram is shown in Figure 11a. A similar sample was autoclaved before addition of labeled TCE (Figure 11b). Vinyl chloride and dichloroethylenes produced in this experiment were shown to be labeled with ^{13}C by the presence of peaks at m/e 63 and 65 for vinyl chloride and at 62 and 97 for dichloroethylenes. This experiment confirmed the formation of vinyl

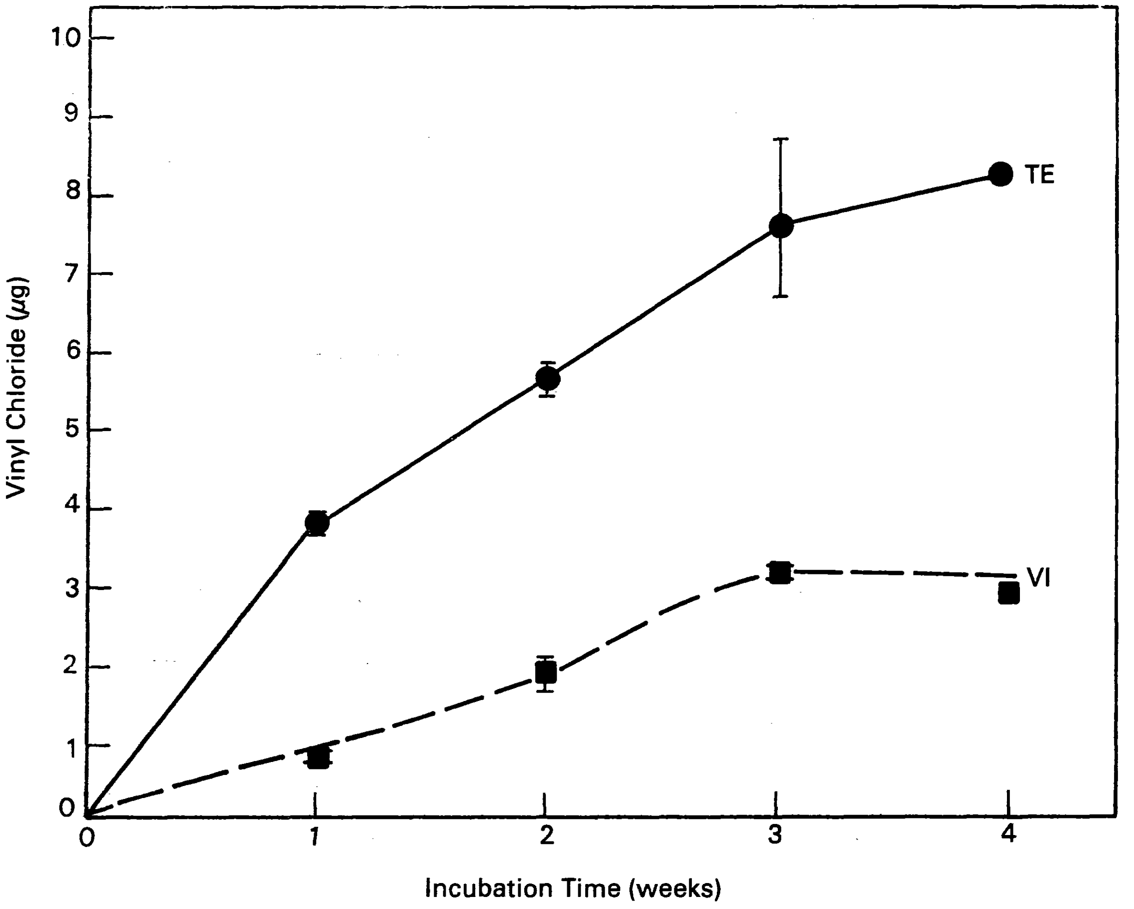
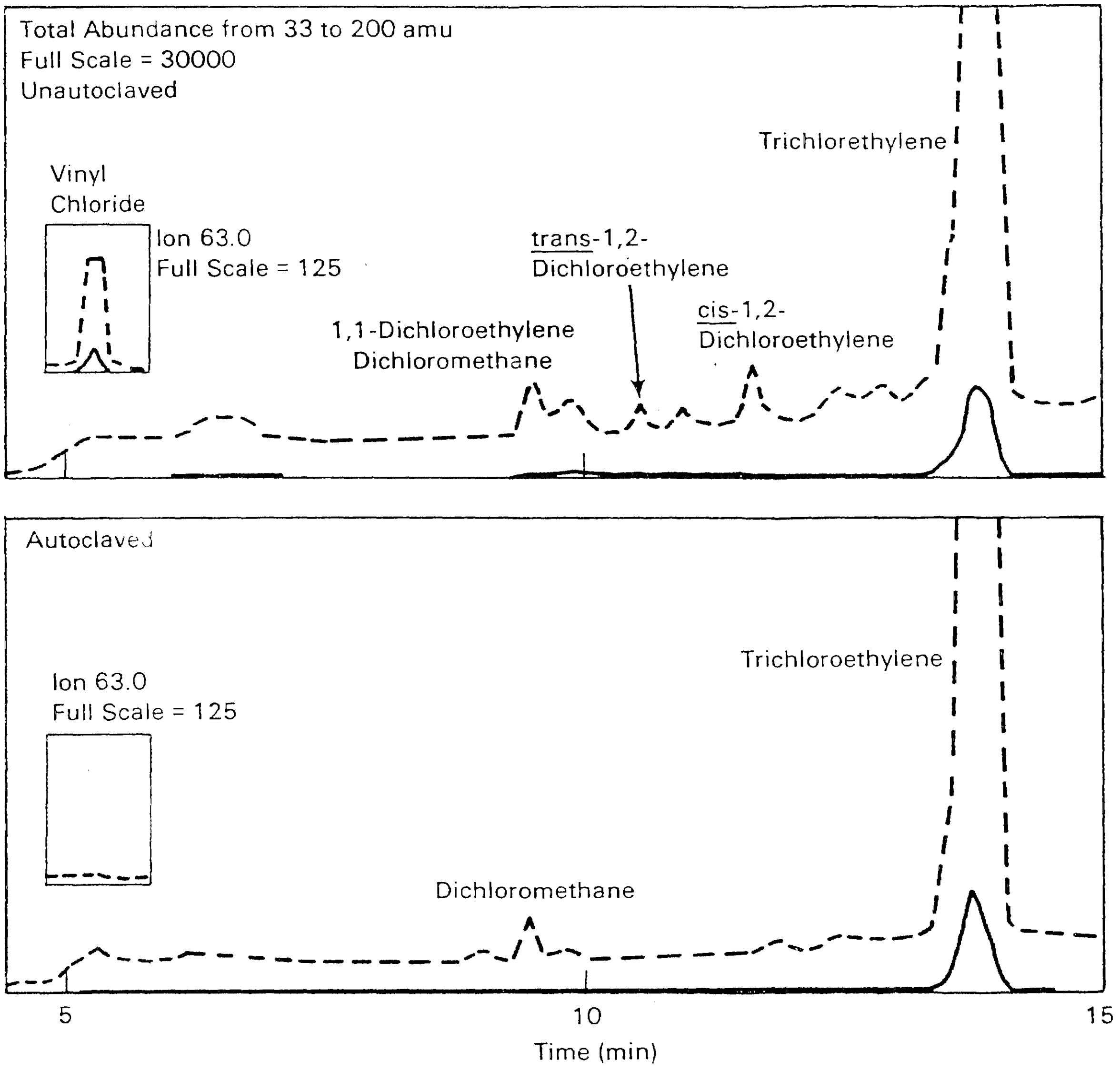


FIGURE 10. Production of Vinyl Chloride from 1,1-Dichloroethylene (Vinylidene chloride, VI) and 1,1,1-Trichloroethane (TE) During Incubation with Sewage Sludge.

FIGURE 11 (a and b). Purge-Trap Analysis of Products from Labeled TCE Incubated with Richland Sewage Sludge



chloride from TCE via dichloroethylenes by a biological route, and also demonstrated the ability of unexposed and unadapted microorganisms to perform the conversion. A similar experiment was performed using sewage sludge spiked with 1,1,2-trichloroethane (unlabeled), and the formation of vinyl chloride shown by GC/MS (peak at m/e 62). Confirmation that chlorocarbons can be converted to vinyl chloride was obtained by incubation with sewage sludge at two temperatures (35 and 55°C). The typical result in the case of 1,1-dichloroethylene is shown in Table 19. Because of lower VC production at 55°C, and because the temperatures at the landfill sampling locations were lower, all subsequent experiments were performed at 35°C. An additional point to note in the results of these preliminary incubation experiments is that for the first experiment, vials were stood upright (R-1-120-). This apparently led to a gradual loss of volatile organic compounds, noticeable after about 3 weeks, by diffusion through the septa; in all subsequent experiments the vials were inverted (septa at bottom), and the problem never recurred.

Table 19: Vinyl Chloride Formation from 1,1-Dichloroethylene.

Temperature (°C)	Incubation Time (days)	Vinyl Chloride Produced (μg)
35	21	2.99
55	25	0.40
55*	25	0.31

* Samples from anaerobic digester.

Chlorocarbon Incubation With Site A Landfill Material:

These experiments were begun according to the procedure given in the experimental methods section within 24 hr of the landfill material being received at Battelle. The most immediate activity was the anaerobic transfer of weighed amounts of landfill material to glass vials for incubation or storage, and analysis of landfill gas samples. This required setting up a large number of vials, as described in the "Materials and Methods" Section.

Experiments performed with landfill material were not straightforward or without problems. After several days incubation, especially of the A-2-16 sample, it was noted that the sample vials were toppling due to pressure build-up causing the septa of the inverted vials to bulge out. Several vials developed pressures in excess of 60 psi and exploded before they could be vented (these were # A-2-16-4, 7, 9, 11, 15, 18, 20, and 22). To prevent all of the sample vials from exploding, the vials were vented after 1 and 2 weeks (vial # 3, 5, 6, 8, 10, 16, 17, 19, 21) and purge-trap analyses performed after 3 weeks. In addition, a sequence of 8 purge-trap analyses was performed on one sample vial. GC/MS analyses were performed on some of the vent samples. For example, vial # A-2-16-16 which was spiked with ^{13}C-TCE, was extensively analyzed, with the results shown in Table 20:

Table 20: Gas and Purge-Trap Analysis of Sample A-2-16-16.

Incubation Time (Weeks)	Analysis Method	Chlorocarbon Component			
		VC	VI	CD	TCE
1	Direct gas, GC/MS	0.002	<0.05	<0.05	0.5
2	Direct gas, GC/MS	0.003	<0.05	0.2	0.2
3	Purge-trap, GC/MS	0.16	0.2	>15	0.3
5.5	Purge-trap, GC/MS	0.04	0.2	>15	<0.05
5.5	Repeat, same day	-0-		13	
5.5	Repeat, 5 times	-0-		<0.5	

Concentrations are in µg.

VC = Vinyl chloride; VI = Vinylidene chloride (1,1-Dichloroethylene);
CD = cis-1,2-Dichloroethylene; TCE = Trichloroethylene

GC/MS responses of these individual compounds are not linear with concentration. Quantitation cannot be achieved without time-consuming calibrations. The result from multiple purge-trap analyses of the same sample demonstrates that landfill material retains chlorocarbons quite strongly, and to remove for example, cis-1,2-dichloroethylene to a level of below 0.5 µg per purge required eight purges on the same sample. We demonstrated a recovery for vinyl chloride on 100 +/- 2% on a single purge-trap pass, and did not attempt further quantitation of other compounds as it was beyond the scope and objectives of the project.

Labeled vinyl chloride production was noted for all remaining Site A landfill sample vials inoculated with labeled TCE. Actual amounts of vinyl chloride in selected samples were calculated. These results are shown in Table 21 (quantitation on all samples was not performed for the reasons given above):

Table 21: Vinyl Chloride Production from Site A Landfill Samples

Sample ID	VC Produced (g)	Incub'n. (days)	Sample ID	VC Produced (g)	Incub'n. (days)
A-1-3-2	-0-	27	A-2-6-1	-0-	27
A-1-3-3	-0-	27	A-2-6-8	0.17	39
A-1-3-6	0.005	34	A-2-6-21	0.01*	19
A-1-3-12	0.01	26	A-2-16-1	0.01	19
A-1-3-14	0.01	26	A-2-16-5	<0.002	26
A-1-3-16	0.05*	26	A-2-16-8	0.03	21
A-1-3-20	0.10*	19	A-2-16-14	0.02	26
A-1-10-2	-0-	27	A-2-16-17	0.07*	26
A-1-10-9	0.16	39	A-2-16-19	0.07*	26
A-1-10-22	0.04*	19	A-2-16-21	0.20*	19

* - Labeled TCE used, labeled VC produced.

In addition, gas samples obtained by venting overpressured vials were analyzed by direct GC/MS injection. These data are qualitative only, but demonstrate the rapid formation of vinyl chloride (within 2 weeks) in the Site A samples (Table 22):

Table 22: Vented Gas Analysis from Site A Samples After 1-2 Weeks

Sample ID	VC Produced	Sample ID	VC Produced	Sample ID	VC Produced
A-2-16-**	Week 1,2		Week 1,2		Week 1,2
2	-	8	+,+	14	,+
3	-	10	+,	17	+,
5	-,-*	12	+,+	19	,+
6	-,-	13	+,+	21	,+

* Analyzed after 1,2 weeks. Samples 1-6 were chlorocarbon-free blanks. "-" indicates absence of VC, "+", presence; blank indicates not analyzed. VC from samples 17, 19, and 21 was labeled, from labeled TCE.

Figure 12a clearly shows the formation of ^{13}C-labeled vinyl chloride from labeled TCE after incubation with Site A landfill material. The ion at m/e 63 is characteristic of labeled VC, coupled with the VC mass spectrum obtained at the same time.

Chlorocarbon Incubation With Site B Landfill Material:

These experiments were also begun according to the procedure given in the experimental methods section within 24 hr of the landfill material being received at Battelle. The most immediate activity was the anaerobic transfer of weighed amounts of landfill material to glass vials for incubation or storage, and analysis of landfill gas samples. This required setting up a large number of vials as listed in the previous section (Materials and Methods).

Compared to the material from Site A, landfill samples from Site B were incubated without problems. There were few cases of excessive gas production, and no vials exploded, although some had to be vented.

Labeled vinyl chloride production was noted for all remaining Site B landfill sample vials inoculated with labeled TCE. Actual amounts of vinyl chloride in selected samples were calculated. These results are shown in Table 23 (quantitation on all samples was not performed for the reasons given above for Site A samples):

Table 23: Vinyl Chloride Production from Site B Landfill Samples

Sample ID	VC Produced (μg)	Incub'n. (days)	Sample ID	VC Produced (μg)	Incub'n. (days)
B-1-3-7	0.17	32	B-2-3-8	0.23	27
B-1-3-9	0.45	45	B-2-3-19*	0.05	21
B-1-3-16	0.29*	21	B-2-3-20*	0.10	21
B-1-3-18	0.04*	21	B-2-10-5	-0-	20
B-1-3-19	0.10*	21	B-2-10-8	0.30	27
B-1-3-20	0.10*	21	B-2-10-9	0.25	22
B-1-10-16	0.06*	21	B-2-10-10	0.06	22
B-1-10-20	0.11*	21	B-2-10-16*	0.04	21
B-2-3-6	-0-	20	B-2-10-19*	0.05	21

* - Labeled TCE used, labeled VC produced.

FIGURE 12. Landfill Samples Spiked with ^{13}C-Trichloroethylene

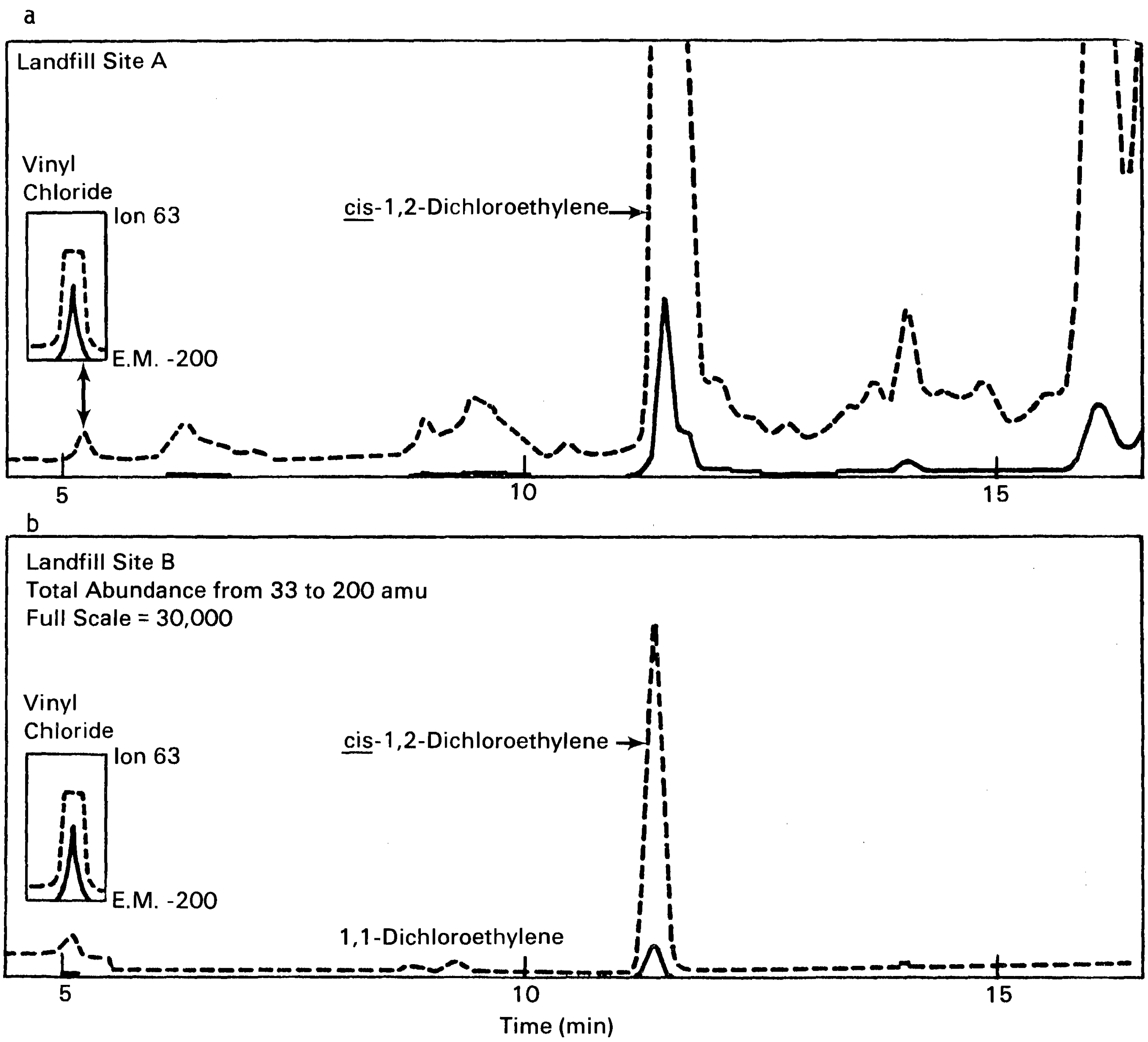
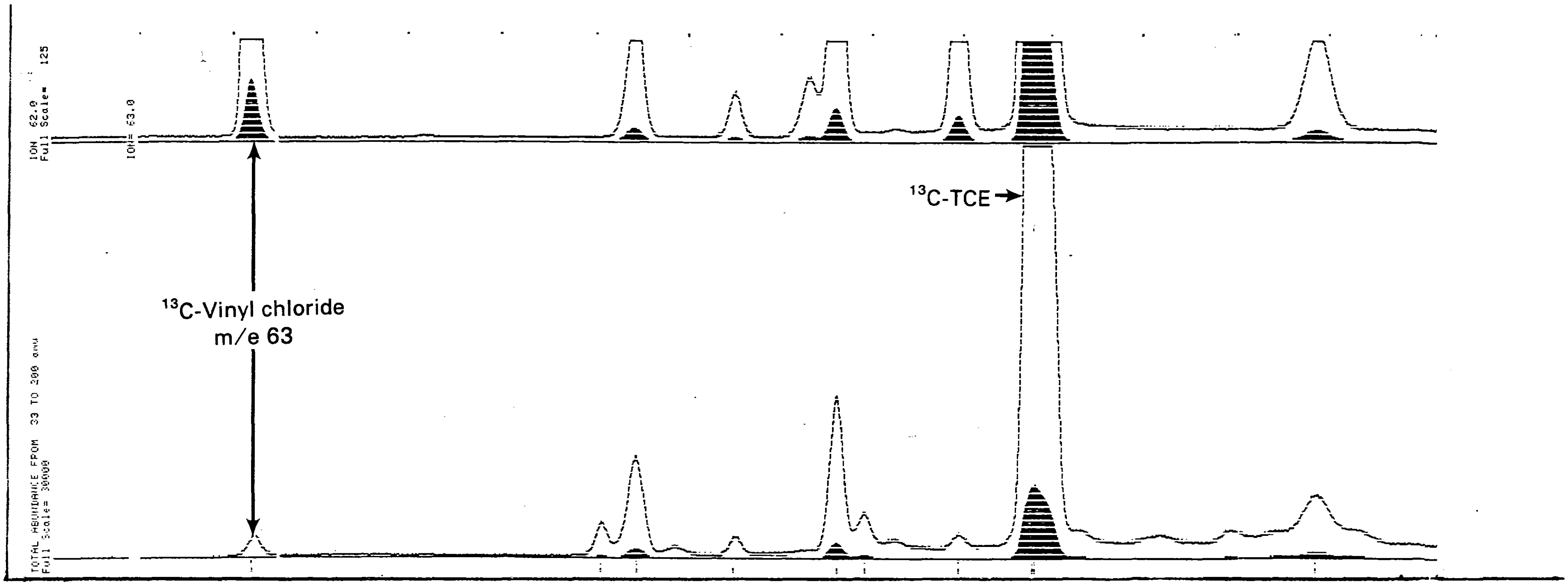


Figure 12b clearly shows the formation of ^{13}C-labeled vinyl chloride from labeled TCE after incubation with Site B landfill material. The ion at m/e 63 is characteristic of labeled VC, coupled with the VC mass spectrum obtained at the same time.

ISOLATION OF VINYL CHLORIDE-PRODUCING METHANOGEN:

Work with samples in vials has shown that methanol can be used as a substrate by the organisms which produce vinyl chloride from chloroethylenes. By using methanol as a carbon source, most of the landfill organisms were selected out as they cannot metabolize this compound. A 2 liter fermentor was used in the following culture isolation experiments. One of the advantages of this approach is that large amounts of the desired organism become readily available. The slow growth rate of methanogens and the slow conversion rate of TCE to vinyl chloride require large numbers of the organisms to be present in order to observe product formation in a reasonable time period. An anaerobic methane-generating population was established from vial samples grown on methanol. The methane: carbon dioxide ratio formed by this culture was 2:1, which is expected for methanogen cultures using methanol as the sole carbon source. After staining and microscopic examination of a portion of this culture, the cell population appeared to be homogeneous (i.e., single species) and were gram-negative cocci (spherical cells). The indications at this stage were that we had a pure culture, although with methanogenic species this assumption is less certain than with other types of bacteria. This culture was able to convert ^{13}C-labeled TCE to ^{13}C-labeled vinyl chloride, as confirmed by GC/MS analysis (Figure 13). From 100 μg of labeled TCE, 1.2 μg of vinyl chloride were produced in 1 week at 35°C. A BBL GasPak anaerobic system was used to monotor contaminant microorganisms. In this system oxygen is removed by reaction with hydrogen over a palladium catalyst, producing water. The hydrogen is generated from sodium borohydride. Since no other reductant besides hydrogen was initially present, the reduction potential was not great enough for methanogens to function. We did not obtain any colonies after incubation in the GasPak system when the culture was plated out on Petri dishes. We also did not observe any colonies after incubation on Petri plates in a normal atmospheric oxygen concentration. Both results suggested that



(Standard GC/MS Conditions Used -- See Methods Section)

FIGURE 13. GC/MS Trace Showing Production of ^{13}C-Labeled Vinyl Chloride from ^{13}C-Trichloroethylene by an Isolated Methanogen Culture.

contamination was low and that mainly methanogens or strict anaerobes were present.

Following these preliminary results, incubation under stringently anaerobic conditions was performed to determine if single species which can produce vinyl chloride could be obtained. The anaerobic system used for these experiments was the roll-tube method (see Methods section for a description of this technique).

Only one type of bacterial colony was observed to grow, demonstrating that the culture was apparently homogeneous (i.e., a single species, although this is not always true with methanogens). To our knowledge, this is the first reported case of isolation of a vinyl chloride-producing methanogen from an actual landfill sample (A-2-16-). The culture is being maintained and replicated in an attempt to obtain sufficient samples for distribution to others and/or to a recognized culture collection.

DISCUSSION

FORMATION OF VINYL CHLORIDE

During the course of the experiments reported here, we obtained and analyzed small landfill material samples, incubated them with labeled TCE, showed the formation of labeled VC and dichloroethylenes, and isolated a methanogen capable of causing this transformation. We also performed experiments to cause various chemical transformations on PVC and chlorocarbons, which uniformly failed to produce detectable amounts of VC beyond those already present as impurities. Killing microorganisms in the landfill samples which normally caused formation of VC from TCE resulted in the complete cessation of this activity. The conclusion from this research is definite: Vinyl chloride is produced from chlorocarbon solvents dumped into landfills through the action of methanogenic bacteria. This may not be the only route, however. Within the limits of error of our experiments we could not completely eliminate other possibilities, but these are minor contributors to the overall VC formation.

This conclusion is true for the landfills we sampled, which were both municipal landfills taking no hazardous waste. The amounts of vinyl chloride present in the headspace gases above the landfill samples on receipt corresponded roughly with the degree of solvent dumping likely to have occurred, although due to loss of volatiles during a brief exposure of the samples to air prior to packing, this is only a qualitative observation. (Site A accepted some industrial waste, and Site B did not; Site A had 5 ppm of VC in the headspace gas, Site B had less than 1 ppm). Reportedly, gas samples taken above hazardous waste landfills where large quantities of chlorocarbons have been dumped contain much larger amounts of VC, in excess of legally mandated exposure limits.

The following discussion is based on our results compared with those of others, and is in support of the basic conclusions stated above.

EXPERIMENTAL APPROACH

The basic objective of the research as stated previously was to identify the source(s) of observed VC emissions from landfills in California. The simple nature of the problem belied the difficulty in obtaining a direct solution. Various experimental approaches were considered. Previous and ongoing research by several groups (notably those of Parsons in Florida and McCarty in California) implicated microorganisms in the formation of VC, and more specifically, anaerobic bacteria. The ability of some microorganisms to dechlorinate chlorocarbons anaerobically has been recognized for some years (e.g., Kobayashi and Rittman, 1982). It would therefore have been logical to accept the conclusions of these groups, and to begin with anaerobic bacteria and use them to demonstrate VC formation from chlorocarbons. Since scientists like to work with defined systems, for obvious reasons, one approach would have been to obtain cultures of various anaerobes and incubate them with chlorocarbons. VC formation could then have been demonstrated and applied by implication to landfill conditions. The difficulty of this approach is that to obtain proof of the ability of the anaerobes to form VC in landfills, the identical species would have had to be isolated from landfill material. Complete and accurate species identification of anaerobes is notoriously difficult, and for this reason we abandoned the approach of beginning with a defined system (anaerobe/salts medium/chlorocarbon) in favor of the undefined system of using actual landfill samples. Reversal of the approach described above would have led to isolation of a VC-producing anaerobe, which could then be identified. This approach of course was the one actually used, although identification of the exact species of anaerobe has not yet been achieved.

Identification of one route for VC formation in landfill material is a positive step, but not the only one. From the point of view of California state agencies, it was also necessary to show the existence or approximate contribution of other mechanisms to the overall picture. A major consideration in this type of work is the fact that there is frequently a discrepancy between what is actually and what is reportedly dumped in landfills. The major concern in this regard is the possibility for illegal dumping in the past of PVC production sludges, at a time when the extreme toxicity of VC was not recognized, and when these sludges contained large amounts of residual monomer (e.g., Markle et.al. (1976)). A further possibility is the obvious one of depolymerization of PVC itself with the formation of VC monomer. Research into these questions led to the conclusion that release of VC by these mechanisms in the landfills we sampled is inherently unlikely. For the first possibility (PVC production sludge dumping), reference to Appendix B shows that PVC production in the State of California and neighbouring States is small; furthermore, illegal dumping would most likely take place at hazardous waste landfills. It is difficult to imagine a clandestine dumping of such toxic materials at municipal landfills such as were sampled by us. As for depolymerization of PVC, considerable effort over the years has gone into identification of the decomposition mechanisms of this important plastic. The direct depolymerization occurs only to a trivial extent (parts per million of VC), and a dehydrochlorination and cyclization is the primary mechanism. Even this only occurs at elevated temperatures likely to occur only rarely under spontaneous combustion conditions. Hence we eliminated PVC and its precursors as likely sources of the VC we observed in our municipal landfill samples.

A further possibility which we were not able to exclude based on our research is the slow leaching of VC monomer from "old" plastics. Samples from our laboratory contained over 300 ppm of VC monomer, while "new" samples contained about 1% of this level. There would have been no reason to refuse waste PVC in either landfill A or B ten years ago, and the same applies to other PVC-type plastics such as household wrap. To determine the degree to which leaching contributes to the overall VC production, long-term studies would be needed to (a) analyze landfills thoroughly to determine the PVC content, (b) analyze the PVC to determine the average VC content, and (c) determine the average water flow and leaching rates. This of course would allow an estimation of the VC contribution to groundwater; further work would have to be done to estimate the transfer to landfill gases, which is a complex function of gas generation rates, organic composition, and other factors. A best guess based on our results is that the contribution from PVC and other plastics is certainly less than 5% and probably less than 1% of the total VC measured.

While production of VC from PVC is unlikely for the reasons given above, the same is not true of VC production from chlorocarbon solvents. These are widely used and ubiquitous, and are found in degreasers, thinners, paints, duplicating fluids, dry cleaning solvents, and a host of other materials in common use. Such materials certainly find their way into municipal landfills in both household and industrial waste. In the latter case, the presence of metal fabrication, electronics, and similar industries in Southern California could have led to the observed higher levels of chlorocarbons in Site A than in Site B.

The formation of VC from chlorocarbons seemed a priority to be the most likely and major source. However, there remained the possibility that some unsuspected mechanism could be implicated. Just because a mechanism appears likely does not necessary imply that it occurs or is the only contributor. Hence, we devised a series of chemical experiments based on heat and radiation, which could also possibly have produced VC from chlorocarbons. We did find that trichloroethane could be converted into 1,1-dichloroethylene, but found no evidence for the formation of VC by pyrolysis, photolysis, or catalytic formation from ethylene and hydrogen chloride.

Having designed our experiments to eliminate formation of VC from PVC and by chemical means, the way was clear to investigate the biological route from chlorocarbons. As discussed in the text, sewage, landfills, and related anaerobic environments (not compost piles, which are aerobic) contain many representatives of three major classes of microorganisms. Generally, these include organisms which convert polysaccharides (cellulose, hemicellulose) to acids, acetogens which produce acetic and butyric acids from other non-polymeric compounds, and methanogens which produce methane and carbon dioxide from acetic acid. From the structural similarity between VC (chloroethylene) and acetic acid, (both C_2 compounds) the methanogens seemed the most likely candidates. In fact, by using methanol as a carbon source for our experiments we selected for methanogens, and since VC was produced in all cases from TCE and other chlorocarbons, the assumption was shown to be correct. It does not preclude other non-methanogenic organisms from also producing VC. Had we used glucose or an organic acid as a carbon source we would have had a much wider variety of anaerobes growing in the incubation experiments, with correspondingly complicated results. This is because the major metabolic product of one class becomes the growth substrate (carbon source) for the succeeding class.

Since the beginning of the decade, when the ability of anaerobes to dechlorinate organic compounds was recognized, our understanding of the conversion route has been getting gradually more complex. Beginning with a linear conversion of tetrachloroethylene, for example, through TCE, all 3 possible dichloroethylenes, and then to VC, the route has been expanded. Figure 14 shows the current understanding based on the work of Parsons and Barrio-Lage (1985), and Barrio-Lage et.al.(1985). Vogel and McCarty (1985) have recently extended this by showing the "mineralization" of VC to carbon dioxide. In our work, the reversibility of the transformation of 1,1-dichloroethylene to VC has been shown by experiments in which VC gas was added, and 1,1-dichloroethylene formation observed. A further clarification of the literature relates to the ubiquity of the organisms responsible: By using chlorocarbon-free sewage sludge and showing formation of VC from a range of chloroethylenes and chloroethanes, we demonstrated that the ability of methanogens to metabolize chlorocarbons is inherent, not acquired (i.e., it is constitutive and not adaptative in nature). In going one step further and isolating a bacterium capable of performing the transformation of labeled TCE to labeled VC while growing on methanol, we have opened up the opportunity for other workers in the field to work with defined systems using this organism. (This isolate is the property of the ARB and was derived from landfill Site A; we hope that it will be made available for further research.)

In performing the experiments required to derive the above statements and conclusions, it was necessary to deviate slightly from strict scientific protocol and to make choices regarding which analyses to perform and in what degree of detail. We emphasize that this was done with the realization that the results would be indicative (although defensible) rather than comprehensive. For example, during the course of this study, we obtained a total of 12 landfill samples plus two sewage sludge samples. Each sample was subjected to various treatments defined in the Methods section, requiring a total of 34 vials for each sample. This total includes only TCE, 1,1-dichloroethane, or 1,1,1-trichloroethane and labeled TCE as the chlorocarbon substrates. A

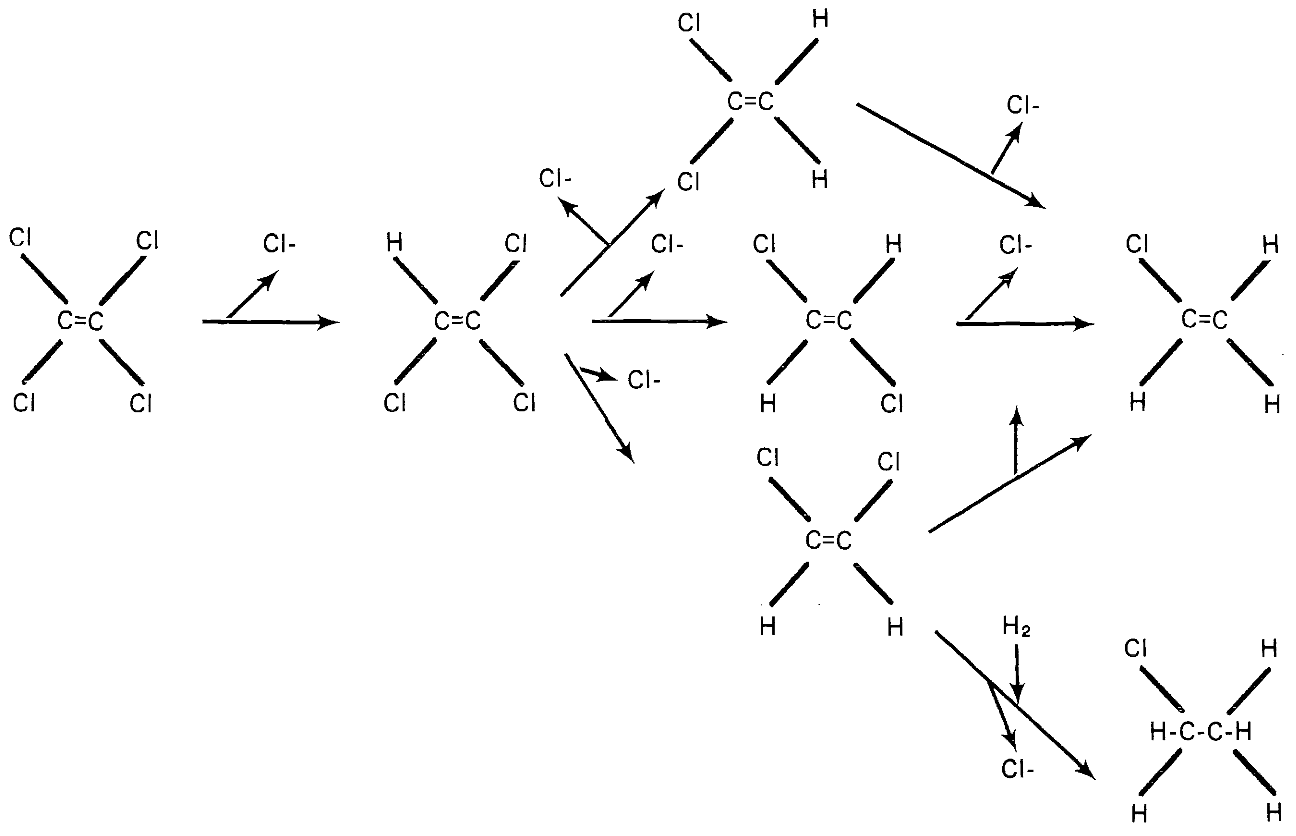


FIGURE 14. Reductive Dechlorination Pathway for Chloroethylenes in Soil (after Parsons and Barrio-Lage, 1985; Barrio-Lage *et.al*., 1985).

complete list would have included all two-carbon chlorocarbons, over a dozen in all. The potential number of vials for analysis in a complete experimental matrix would therefore have been 14 x 94, or over a thousand. To perform a purge-trap and GC/MS analysis of each vial in this matrix would have been beyond the ability of the project to support, even using the basic purge-trap system. Further, the purge-trap system was designed to give an accurate value for VC, and did not provide for complete volatilization of higher chlorocarbons from the sample matrix, which would have further extended the time required and the analytical difficulty. The GC analysis was based on total ion peak heights, and took into account different GC responses for the different compounds. The nonlinearity of the GC/MS analytical system, the large concentration range encountered, and use of the total ion monitor make the results at best semi-quantitative for compounds other than vinyl chloride. These approximations are discussed here to point out that the numerical data presented in the Tables are indicative rather than definitive. They demonstrate conclusively that VC is formed from TCE, for example, but are not accurate or complete enough to provide a basis for calculation of reaction rate constants. Bearing in mind the heterogeneous and variable nature of the landfill material, and the objectives of the project, we felt that these approximations were both necessary and reasonable, but we do not intend to misrepresent the data as more accurate than it really is. The basic conclusions of the study are not affected, notwithstanding the above reservations.

EMISSION OF VINYL CHLORIDE FROM LANDFILLS

Analytical data on landfill emissions of VC is rapidly being accumulated, and it is apparent that the problem is widespread, if not universal. Whether or not VC emissions pose a health threat is moot. At the levels we detected from Site A and Site B, there seems little risk to health even over the landfill. However, this assumes that the VC is not allowed to accumulate in the dark and is allowed to blow away or be decomposed by sunlight. There is a potential for accumulation which should be watched with care: By covering a landfill for the purpose of landfill gas collection, positive pressure is sometimes generated. This can drive landfill gases away from the landfill and into basements in neighbouring structures. Basements and cellars being often dark, there is little potential for decomposition by solar UV light, and VC accumulation to high levels is a possibility. Hence, the most popular method for controlling landfill emissions could conceivably enhance rather than reduce the risk to health.

If Site B is a typical municipal landfill receiving typical amounts of chlorocarbons from mainly houshold refuse, then VC concentrations in the air over the landfill are unlikely to reach 1 ppm. Sites accepting chlorocarbon wastes, both municipal and hazardous (e.g., in "Silicon Valley") are more likely to pose a problem. This is especially true if the sites are old or abandoned, have received large amounts of chlorocarbons in the past, and may have been built over.

POSSIBLE REMEDIAL ACTIONS AND ADDITIONAL RESEARCH

The standard approach to control of gases being emitted from landfills is to provide a cover and to pump out the gases and burn them. While this approach generally works, it may lead to dispersal of VC outwards from the landfill because of the positive pressure generated by the cover, and the high solubility of VC in water. As mentioned above, this raises the possibility of forcing VC into basements where it could possibly accumulate. On the other hand, in the absence of any cover the VC may be able to reach air and sunlight where it is rapidly destroyed, but this is a "do-nothing" approach which does not solve the problem. The actual action taken (i.e., cover or no cover) may depend on the concentration of VC over the landfill, the proximity to dwellings, factories, and schools, and the amount of other gases being generated. In an active landfill where anaerobic digestion is proceeding rapidly, high emission rates of methane and carbon dioxide may require active gas removal and combustion to prevent it accumulating in nearby buildings. The alternative approach would be to aerate the landfill to blow the VC into the atmosphere and prevent the action of anaerobic organisms, but this is impractical because it would also prevent anaerobic digestion and decay of refuse, which is the major purpose of a landfill. Composting of refuse by forced air aerobic degradation is currently becoming popular, but this would have the effect of blowing volatile chlorocarbons into the air. These would then have to be collected by covering the composting operation, which is expensive. It appears that almost any simple solution to the VC emission problem would have undesirable consequences.

The problem arises because of the presence of chlorocarbons in landfills. Even if all dumping of chlorocarbons could be stopped today, the residues in landfills across the country would continue to be degraded to VC for an unknown period, possibly many years. However, the amounts of VC produced would gradually decrease. The question of remedial actions therefore falls into two categories:

(a) Dealing with the current problem from pre-existing chlorocarbons;

(b) Avoiding future problems by preventing chlorocarbon dumping.

In order to approach (a), the rate of degradation of various chlorocarbons of interest under landfill conditions needs to be known. An answer must be found to the question: "For how many years after dumping a particular chlorocarbon will problematical concentrations of VC continue to be emitted?" This also involves research into transport rates of VC upwards in landfills. Chlorocarbons are toxic to most microorganisms and most of them are highly insoluble in water, so the degradation rate is unlikely to be a linear function of chlorocarbon concentration. Little useful data is available on this subject. In the absence of hard data, it is obvious from the continued emission of VC from inactive landfills that the chlorocarbon half-lives are measured in years. We estimate that 20-30 years could be required, though this is little more than a guess. The information is necessary in order to estimate the required service lifetime of possible remedial measures, since the economics of various approaches are time-dependent.

At present, almost the only practical solution to control is to cover the landfill and burn the collected gases. This technology exists, but it is expensive and incomplete. Covers vary from sandy soil of high porosity to impermeable layers of plastic. The equipment required (blowers, pipes, incinerators) is subject to corrosion and breakdown. A decision to apply a gas recovery/destruction system to a particular landfill would not be easily made as it would involve a considerable amount of time, planning, and expense.

Also, it is difficult to apply to landfills which are still in use or which are geographically disperse or on uneven terrain.

Apart from research into improvements in landfill gas recovery technology which are sorely needed, there is a potential approach based on biotechnology which is being applied with some success in similar situations. This is the technique of _in situ_ biodegradation of selected hazardous organic compounds. Only a few years ago it was thought that, for example, PCB's would continue to cause problems in the environment for centuries because of the high resistance to degradation and low solubility in water of these substances. Laboratory research into isolation and adaptation of microorganisms capable of degrading PCB's has led to the selection of strains with a high capacity for PCB degradation. Spraying a culture of these organisms onto the surface of a landfill, with an added carbon source (acetate, glucose) for metabolic support, leads to relatively rapid PCB degradation as the organisms adapt to the new conditions and multiply.

Applying this approach conceptually to the problem of VC production from landfills could lead to the selection of an organism capable of completing the degradation of VC aerobically to carbon dioxide and water. (An aerobic organism capable of using VC as its sole carbon source has recently been reported, so such species do exist.) The alternative approach would be to select for an anaerobic organism with a high tolerance and degradation capacity for chlorocarbons. In the one case, an aerobic organism would be sprayed onto the landfill surface to capture and oxidize VC being emitted, and in the other a culture would be inoculated deep in the landfill to attack the existing chlorocarbons. Possibly both approaches could be successful, but research is in an early stage at present, and should be continued and expanded. At best, the approach could lead to an inexpensive alternative to landfill gas collection and incineration in some cases.

The second approach is to prevent future chlorocarbon dumping. This could simply be legislated, as chlorocarbons are easy to detect by GC and as industrial waste is more and more frequently analyzed on site before dumping is permitted. The problem with this approach is that chlorocarbons are used because they are needed, and preventing their disposal will not remove the need. Rather, this approach would simply cause the waste solvents to be disposed of in less obvious ways and places than legal landfills. In fact, current law already greatly restricts industrial solvent dumping and encourages on-site recycling and conservation. Research is therefore required into the development of non-toxic alternatives for current chlorocarbon uses, and also into ways of capturing and recycling chlorocarbons for which alternatives cannot be found. The major application for chlorocarbons industrially is in degreasing; it seems likely that other solvents exist which would be suitable for this application and which are relatively non-toxic, biodegradable, and which are not converted to VC. Unfortunately, most of them are flammable, which was a major reason for selection of the non-flammable chlorocarbons in the first place.

The key to the recycling of these solvents may already exist: Some years ago, as toxicity data on TCE and perchloroethylene was developed, it was feared that exposure to these solvents in the dry-cleaning industry was a health hazard. Exposure limits were therefore lowered and stringent recovery systems applied (this was also done for economic reasons - these solvents are expensive). The system in use at present involves a charcoal trap, which is highly effective. When saturated, the solvents are distilled out and reused. Very little dry cleaning solvent is now lost to the environment, mainly in the form of waste charcoal which can be incinerated. Application of this technique to degreasing would greatly reduce the loss of chlorocarbons to the environment. Other uses, including various household applications, involve very small amounts of chlorocarbons relative to the total and can probably be ignored.

ACHIEVEMENT OF PROJECT OBJECTIVES

The project objectives were defined in our original proposal as accepted by the ARB, and were all met. For reference, these objectives were:

- Identify materials present in landfill sites by direct sampling which could be precursors for VC;

- Determine oxygen concentrations at different depths in selected landfill sites, as a necessary prerequisite to hypothesizing a VC formation mechanism;
- Design experiments to determine whether the formation mode for VC is chemical, biological, photochemical, or some combination of these;
- Verify experimental procedures for determination of VC concentration;
- Attempt to identify the specific chemical precursor(s) for VC by demonstrating VC formation under landfill conditions;
- If a biological route or step is involved, attempt to identify the specific organism(s);
- Perform the above experiments in a timely manner consistent with project funding, quality assurance, and record-keeping requirements;
- Report the results to the California Air Resources Board with appropriate conclusions and recommendations.

CONCLUSIONS AND RECOMMENDATIONS

Our major conclusions and recommendations from this study were presented at the beginning of this report; hence there is no need to duplicate them here, except to comment that the work performed in this study taken together with that of other workers highlights a problem with chlorocarbon dumping. From this point in time, additional research will be performed to further delineate and define the extent of the problem, leading hopefully to a solution acceptable to industry, government, and the general public. This should in turn lead to a safer work-place, residential, and outdoor environment.

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GLOSSARY

The following is a list of terms, abbreviations, and symbols used in the text and which may require explanation:

Acetogen	Type of anaerobic bacterium which produces acids from sugars.
ARB	Air Resources Board, the sponsoring organization for this project.
FID	Hydrogen Flame Ionization Detector used in GC.
GC	Gas Chromatography.
GC/MS	Combined Gas Chromatography/Mass Spectrometry (the mass spectrometer functions as a GC detector).
HPLC	High Pressure Liquid Chromatography (requires especially pure solvents).
ICP	Inductively Coupled Plasma technique for inorganic element analysis.
Methanogen	Type of anaerobic bacterium which produces methane and carbon dioxide from acetate.
NBS	National Bureau of Standards.
PI, PID	PhotoIonization type of GC detector.
TCE	Trichloroethylene, a common dry-cleaning/degreasing solvent.
VOC	Volatile Organic Compound.

APPENDICES

APPENDIX A: SUPPLIERS AND USAGE OF MAJOR CHLOROCARBONS

U.S. Suppliers*:

Company	Location	Capacity/Chemical^{+}					
		VC	PVC	TCE	EtCl2	TCEt	PCE
Air Products	Calvert City, KS	-	200	-	-	-	-
Air Products	Pensacola, FL	-	200	-	-	-	-
Arco	Port Arthur, TX	-	-	-	600	-	-
Borden	Geismar, LA	700	350	-	-	-	-
Borden	Illinopolis, IN	-	320	-	-	-	-
CertainTeed	Lake Charles, LA	-	220	-	-	-	-
Diamond Shamrock	Deer Park, TX	-	-	-	190	-	165
Diamond Shamrock	Convent, LA	-	-	-	800	-	-
Dow	Freeport/Oyster Creek, TX	750	-	120	2700	450	-
Dow	Plaquemine, LA	800	-	-	1700	-	90
Dow	Pittsburg, CA	-	-	-	-	-	50
DuPont	Corpus Christi, TX	-	-	-	-	-	160
Formosa	Baton Rouge, LA	420	-	-	560	-	-
Formosa	Delaware City, DE	-	330	-	-	-	-
Formosa	Point Comfort, TX	580	890	-	-	-	-
Georgia-Gulf	Delaware City, DE	-	150	-	-	-	-
Georgia-Gulf	Plaquemine, LA	1100	700	-	1815	-	-
BF Goodrich	Avon Lake, OH	-	280	-	-	-	-
BF Goodrich	Calvert City, KY	1000	-	-	1000	-	-
BF Goodrich	Deer Park, TX	-	240	-	-	-	-
BF Goodrich	Henry, IL	-	180	-	-	-	-
BF Goodrich	La Porte, TX	1000	-	-	1585	-	-
BF Goodrich	Louisville, KY	-	280	-	-	-	-
BF Goodrich	Pedricktown, NJ	-	340	-	-	-	-
BF Goodrich	Plaquemine, LA	-	180	-	-	-	-
Goodyear	Niagara Falls, NY	-	120	-	-	-	-
Keysor	Saugus, CA	-	50	-	-	-	-
Occidental	Baton Rouge, LA	-	300	-	-	-	-
Occidental	Burlington, NJ	-	250	-	-	-	-
Occidental	Pottstown, PA	-	200	-	-	-	-
Occidental	Pasadena, TX	-	700	-	-	-	-
PPG	Lake Charles, LA	500	-	220	2700	350	200
Shell	Deer Park, TX	840	-	-	1340	-	-

Company	Location	Capacity/Chemical+					
		VC	PVC	TCE	EtCl2	TCEt	PCE
Shintech	Freeport, TX	-	1000	-	-	-	-
Union Carbide	Texas City, TX	-	125	-	-	-	-
Vista	Aberdeen, MS	-	360	-	-	-	-
Vista	Lake Charles, LA	700	-	-	1150	-	-
Vista	Oklahoma City, OK	-	355	-	-	-	-
Vulcan	Geismar, LA	-	-	-	300	200	150
Vulcan	Wichita, KS	-	-	-	-	-	50
Vygen	Ashtabula, OH	-	100	-	-	-	-

[*] Information compiled from Chemical Marketing Reporter.

[+] VC = Vinyl Chloride; PVC = Polyvinyl Chloride; TCE = Trichloroethylene; EtCl2 = Ethylene Dichloride (1,2-dichloroethane); TCEt = 1,1,1-Trichloroethane; PCE = Perchloroethylene (tetrachloroethylene). All figures are in millions of pounds annually.

Uses:

Vinyl Chloride - Polyvinyl chloride production (85%), co-polymers (2%); the remainder is exported. Demand in 1985 was 6.9 billion pounds.

Polyvinyl Chloride - PVC is used in rigid pipe, tubing, and molded fittings (43%), flooring and textiles (10%), siding and accessories (7.5%), coatings and pastes (6.5%), wire, cable, film, and sheet (3.5%), other extrusions (4.5%), bottles (3%), other molding uses (1.5%), phonograph records (0.5%), and miscellaneous uses (6%). Demand in 1985 was 6,700 million pounds.

Trichloroethylene - Vapor degreasing of metal parts (66%), chemical intermediates (7%), domestic uses (5%), the remainder being exported. Demand (1982) was 240 million pounds; 1987 prediction for use was 215 million pounds.

Ethylene dichloride (1,2-dichloroethane) - used to make vinyl chloride monomer (90%), 7% is exported, and the remainder is used in manufacture of other chlorinated solvents, vinylidene chloride, and ethyleneamines. The demand in 1985 was 12.68 billion pounds.

1,1,1-Trichloroethane - used in cold cleaning (40%), vapor degreasing (22%), adhesives (12%), aerosols (10%), electronics (6%), coatings (1%), and miscellaneous uses (4%), 5% being exported. Demand in 1982 was 588 million pounds; 1987 use predicted as 680 million pounds.

Perchloroethylene - used in dry cleaning and textile processing (53%), chemical intermediates (mostly Fluorocarbon F-113)(28%), industrial metal cleaning (10%), miscellaneous uses (4%), and the remainder is exported. The demand in 1985 was 595 million pounds.

APPENDIX B: AMERICAN CHEMICAL SOCIETY PRESENTATION AND PRESS RELEASE

The following is the text of the ACS presentation and press release:

TRANSFORMATION OF CHLORINATED ETHENES AND ETHANES BY ANAEROBIC MICROORGANISMS

R. T. Hallen, J. W. Pyne, Jr., and P. M. Molton

ABSTRACT

The biological transformation of chlorinated ethenes and ethanes to vinyl chloride has been observed in experiments which simulate conditions found in a landfill or chemical waste dump. Experiments employed microbial samples obtained from a municipal anaerobic digester and which had not been adapted to chlorinated solvents. Samples contained in septa capped vials were incubated for one week then spiked with a chlorinated solvent diluted in methanol. Vials spiked with 1,1,2-trichloroethane and 1,1-dichloroethene produced the highest levels of vinyl chloride. Those spiked with trichloroethene isotopically labeled with one C-13 atom produced isotopically labeled dichloroethenes and vinyl chloride. Autoclaved and unspiked vials did not yield vinyl chloride. However, autoclaved vials spiked with 1,1,2-trichloroethane produced 1,1-dichloroethene.

INTRODUCTION

The identification of vinyl chloride as a carcinogen has led to strict emission limits for all industrial uses of the material, which also apply to landfill sites. The existence of vinyl chloride emissions from landfills above the set limits has been known for some years, as has the presence of vinyl chloride in leachate waters. One example was described by Walsh (1) for the Lees Lane, Ohio and Port Washington, New York landfills. Both are municipal landfills, and in the Port Washington facility particularly, no hazardous wastes were permitted and the restriction was reportedly stringently enforced. However, analysis of landfill gases in monitoring wells at these sites over a 2-year period showed the mean vinyl chloride concentration at Lees Lane was 28 ppm (range 0-188 ppm) and at Port Washington it was 15.84 ppm (no range reported). The detection of vinyl chloride at landfills and in leachates where no vinyl chloride-containing wastes were reportedly placed led to initiation of research to determine the source(s) of vinyl chloride emission.

One possible source of vinyl chloride emission from landfills is the biological degradation of chlorinated organic solvents. The anaerobic degradation of chlorinated ethenes and ethanes in groundwater systems has been observed by various workers (2-5). The formation of vinyl chloride in microcosms simulating a groundwater environment was reported to result from the reductive dechlorination of dichloroethenes (2). Dichloroethenes are presumably formed by a similar mechanism from tetra- and trichloroethenes

(3). The transformation of isotopically labeled trichloroethene to labeled 1,2-dichloroethene by soil microbes has been reported (4). In all of the studies, no transformation of chlorinated ethenes was observed when the soil samples or microcosms had been sterilized. The degradation of chlorinated organics by reductive dehalogenation has also been supported by data from studies conducted at solvent recovery facilities, solid/hazardous waste landfills, and solvent contamination near an industrial facility (5). The further away from the solvent sources the higher the proportion of degradation products. It was also noted that the higher the concentration of other organics the greater the degradation of chlorinated solvents. The degradation scheme of chlorinated ethenes and ethanes via reductive dehalogenation is summarized in Figure 1. The existence of other degradation schemes was supported by formation of chloroethane from cis-1,2-dichloroethene and the fact that in no cases can the amount of substrate lost be accounted for by the observed products (2).

Actively decomposing dump sites differ from normal soil conditions because of the higher concentration of degradable organic material and the larger populations of anaerobic microorganisms. The objective of this research was to study the transformation of chlorinated ethenes and ethanes in vials simulating landfills and chemical waste dumps. Because microorganisms from actual landfill core samples were not available at the time of this presentation, experiments were performed using microorganisms from the anaerobic digester at a municipal wastewater treatment facility in which no industrial solvents are added. Many of the organisms in this source should be the same as those found in a landfill since municipal landfills are used to deposit material from sewage treatment facilities.

EXPERIMENTAL

Two methods were initially used to prepare vials for experimentation. Initially, samples were prepared in a glovebag and solutions degassed to remove oxygen. Sample preparation involved placing 30 ml of a 10 percent anaerobic reactor fluid diluted with organic-free deionized water in a 40 ml septum cap vial and spiked with 10 μl of a solution containing a chlorinated compound dissolved in methanol at 10 mg/ml. The second procedure involved placing 30 ml of a 20 percent anaerobic digester solution in the septum cap vial without trying to exclude oxygen. The vials were then incubated for one week allowing the microorganism present to deplete the oxygen then the spike was injected through the septa cap and the vial inverted. Microcosms with no additions or methanol only were prepared in a similar manner. Heat treated microcosms were prepared by duplicate exposure for 20 minutes at 121°C on consecutive days. The vials were incubated in a dark growth chamber kept at 35°C or 50°C for periods of one to ten weeks, when duplicate samples were analyzed by the purge-trap technique.

Microbial activity was monitored by analysis of the headspace gases in the vials. Levels of fixed gases were estimated using a Carle Series 400 AGC gas chromatograph set up for refinery gas analysis. Microbial activity resulted in the loss of oxygen and formation of methane and carbon dioxide. The autoclaved vials showed no loss of oxygen or methane formation and were considered sterile.

The highest available purity of tetrachloroethene, trichloroethene, cis-1,2-dichloroethene, trans-1,2-dichloroethene, 1,1-dichloroethene, 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1-dichloroethane, and 1,2-dichloroethane was purchased from Aldrich Chemical Company. Isotopically labeled trichloroethene containing one C-13 atom was purchased from Burdick and Jackson Laboratories. Vinyl chloride standards at concentrations of 1, 10, and 100 ppm were prepared by Scott Specialty Gases. Chemicals were used as received and purity checked by GC and GC/MS.

The purge-trap analytical techniques used were similar to those reported by Bellar et al. (6). The entire contents of the 40 ml septum cap vials were purged using a needle purge apparatus reported by Dressman and McFarren (7). The traps employed contained 7 cm of Tenax TA backed by 7 cm of Sperocarb. The gas chromotograph employed a 6-foot glass column filled with Chromosorb 101 for the first third and the remainder with Chromosorb 102 (7). This column resolves vinyl chloride from water and the cis and trans isomers of 1,2-dichloroethene (not done on EPA 601 column). A photoionization detector and a flame ionization detector were connected in series, the photoionization detector responding to the chlorinated ethenes and not the ethanes. The gas chromatograph-mass spectrometer employed a similar column with a molecular jet separator for sample introduction.

RESULTS AND DISCUSSION

Initial screening experiments for vinyl chloride formation employed vials prepared by the first procedure and spiked with all of the chlorinated ethenes and ethanes used in this study (spike ≃100 μg). It was found that by six weeks incubation at 35°C vinyl chloride (typically 0.03 to 0.01 μg) was formed from all of the chlorinated ethenes. The highest level of vinyl chloride (0.06 μg) was found at three weeks incubation with 1,1-dichloroethene.

At three weeks the transformation of C-13-labeled trichloroethene occurred producing 1,1-dichloroethene (0.22 μg), trans-1,2-dichloroethene (0.08 μg), cis-1,2-dichloroethene (0.16 μg), and vinyl chloride (0.02 μg) with some loss of the isotopic label. Little change in the concentrations of the chlorinated ethenes was noted after three weeks of incubation, which also corresponds to the time required for the disappearance of the initial methanol spike. Vinyl chloride levels actually decreased between three and six weeks for 1,1-dichloroethene. Incubation of the anaerobic microbes for three weeks with vinyl chloride showed a loss of 40 percent and the formation of 1,1-dichloroethene.

Vinyl chloride (0.44 to 0.01 μg) was also formed from the chlorinated ethanes studied. The highest levels of vinyl chloride (0.44 μg) found for all compounds was after one week incubation with 1,1,2-trichloroethane. The transformation of chlorinated ethanes is exemplified by 1,1,2,2-tetrachloroethane. At six weeks incubation 1,1,2,2-tetrachloroethane was transformed to 1,1,2-trichloroethane (1.8 μg), trichloroethene (4.2 μg), cis-1,2-dichloroethene (8.0 μg), trans-1,2-dichloroethene (4.2 μg), 1,1-dichloroethene (0.42 μg), and vinyl chloride (0.05 μg). Vials incubated at 50°C with the chlorinated solvent spikes also showed vinyl chloride formation after a similar incubation time but the levels were lower than those at 35°C.

The transformation of 1,1-dichloroethene and 1,1,2-trichloroethane was investigated in further detail using vials prepared by the second procedure. Microbial activity was much higher in these vials. Vinyl chloride levels from 1,1-dichloroethene were 1.1 μg at one week and 2.0 μg at two weeks incubation. From 1,1,2-trichloroethane the vinyl chloride levels were 4.3 μg at one week and 5.8 μg at two weeks of incubation.

Blank and methanol only experiments did not produce vinyl chloride. Purge-trap analysis of blanks showed no change with time of incubation but the methanol only experiments produced methanethiol and dimethyldisulfide. Autoclaved vials were prepared with 1-(C-13) trichloroethene and 1,1,2-trichloroethane and compared with controls containing no chlorinated hydrocarbons.

After five weeks growth at 35°C, autoclaved and unautoclaved vials spiked with C-13 labeled trichloroethene were analyzed by GC/MS. The chromatographs are shown in Figure 2 for two samples. Labeled trichloroethene was converted to labeled vinyl chloride (0.1 μg), labeled 1,1-dichloroethene (<0.5 μg), 80% labeled trans-1,2-dichloroethene (<0.5 μg) and 90% labeled cis 1,2-dichloroethene (<0.5μ in the unautoclaved vials with no vinyl chloride formation in the autoclaved vials. A similar comparison is shown in Figure 3 for vials spiked with 1,1,2-trichloroethane. The unautoclaved vials yielded vinyl chloride (2.4 μg) with 1,1-dichloroethene and 1,2-dichloroethane at similar levels. The autoclaved vial did not produce vinyl chloride but produced 31 μg of 1,1-dichloroethene. The transformation of 1,1,2-trichloroethane to 1,1-dichloroethene appears to be independent of microbial activity.

CONCLUSIONS

Chlorinated ethenes and ethanes are transformed to vinyl chloride by anaerobic samples which simulate landfill conditions. The degradation scheme is more complex than that shown in Figure 1. The chlorinated ethanes are transformed to chloroethenes including vinyl chloride. The dechlorination reactions may also be reversible. Higher levels of vinyl chloride were found using 1,1-dichloroethene than from cis or trans-1,2-dichloroethene. Work in this area is continuing with microcosms prepared with actual landfill material.

ACKNOWLEDGMENTS

The authors wish to thank the California Air Resources Board for funding the research under contract #A4-154-32 and the Richland Wastewater Treatment Facility for assistance in acquiring digester samples.

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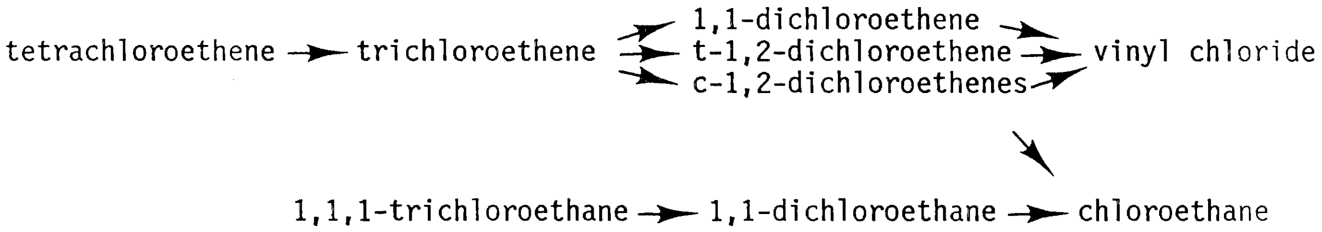

FIGURE 1. Pathways for Dehalogenation of Chlorinated Ethenes and Ethanes in Anaerobic Environments

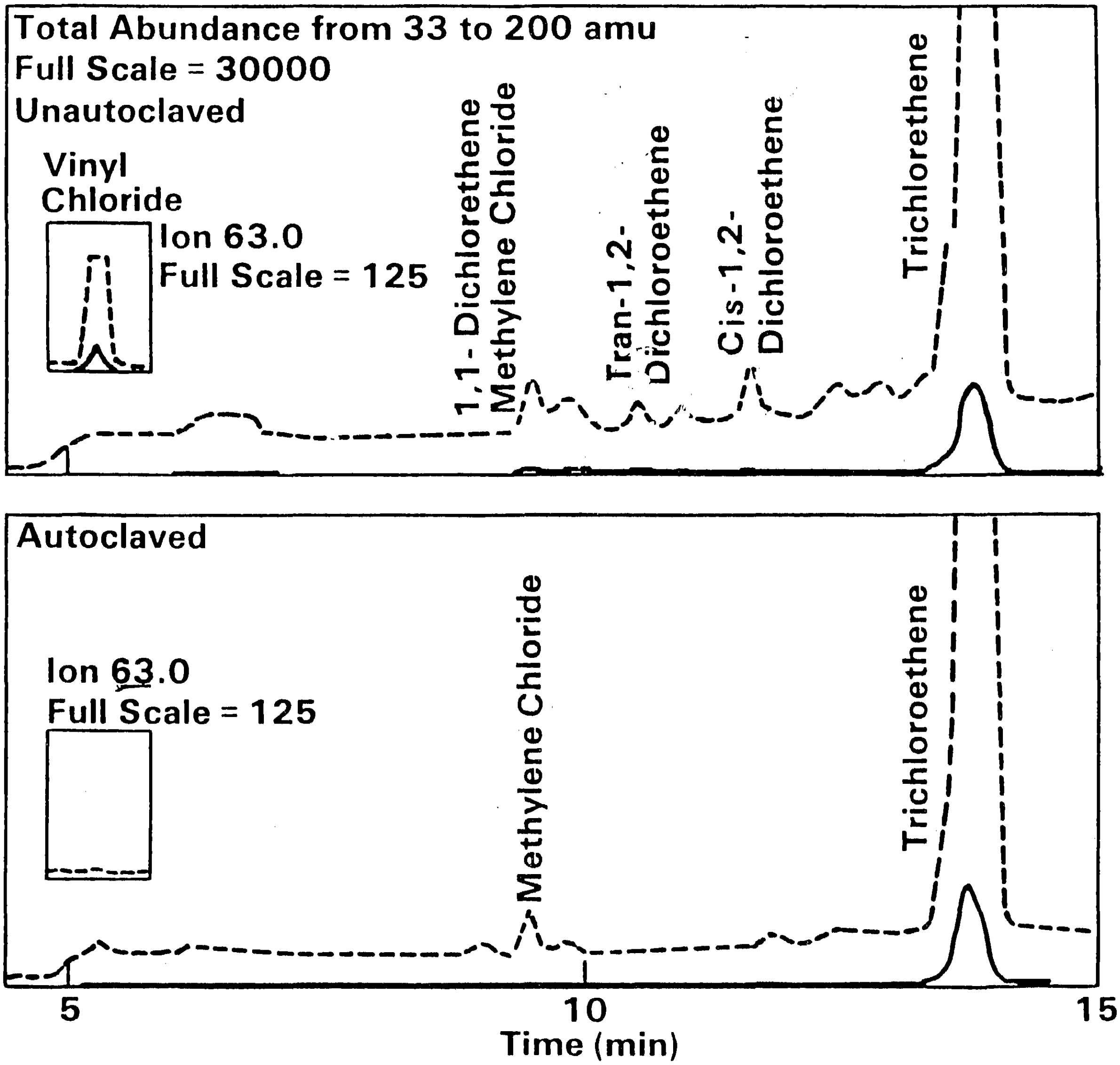

FIGURE 2. GC/MS Chromatographs from Purge-Trap Analysis of Autoclaved and Unautoclaved Vials Spiked with C-13 Labeled Trichloroethene

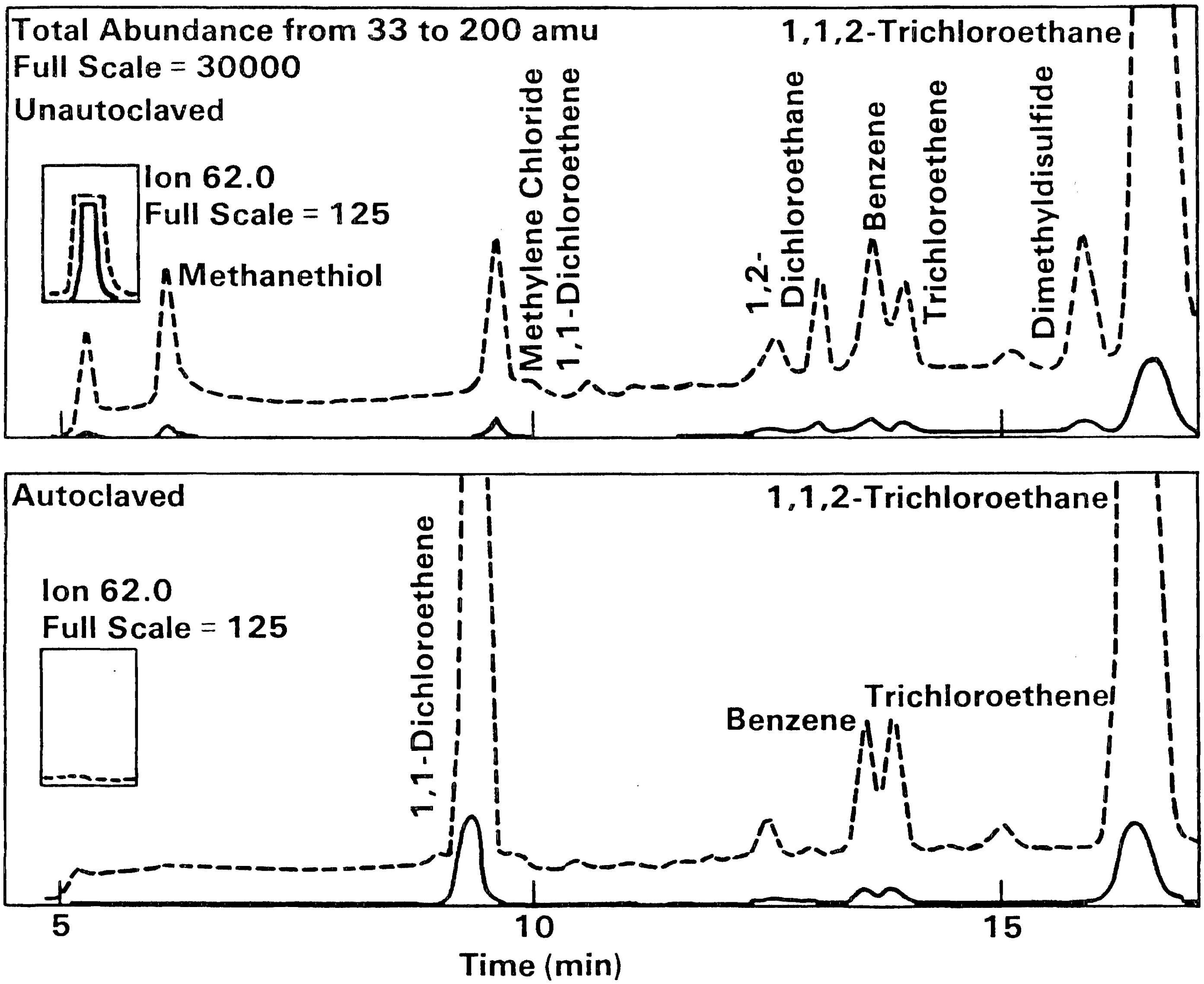

FIGURE 3. GC/MS Chromatographs from Purge-Trap Analysis of Autoclaved and Unautoclaved Vials Spiked with 1,1,2-Trichloroethane

Non-technical Summary:

The Transformation of Chlorinated Ethenes and Ethanes by Anaerobic Microorganisms

Trace (parts per million) amounts of vinyl chloride have been identified in gases emitted from landfills, and in groundwater, even in places where the dumping of vinyl chloride-containing or other hazardous or toxic wastes has never been permitted. Although the amounts are small, vinyl chloride is a carcinogen and the problem appears to be nation-wide. The California Air Resources Board is sponsoring a research project at Battelle's Pacific Northwest Laboratories to determine the source of vinyl chloride appearing in groundwater and landfill gases. The research is being performed by Dr. Peter M. Molton, Dr. John W. Pyne, and Mr. Richard T. Hallen.

Sample material was taken from a landfill site in Northern California, and one in Southern California. Samples were taken from 3 to 10 feet below the cover soil, and contained (among other unidentifiable household and office refuse at various stages of decomposition) dirt, newspapers, grass clippings, glass, and plastic. The samples were then placed in a plastic bag and flushed with gas to remove oxygen to ensure an anaerobic environment for experimental work. This is important because anaerobic bacteria which normally decompose refuse in landfills are considered a primary potential source of vinyl chloride when exposed to substances containing organic chlorine. Small amounts of chlorinated solvents in methanol (a carbon source for the bacteria) were introduced into the experimental vials containing small amounts of landfill material. Various common solvents were used, including trichloroethylene, a dry-cleaning solvent. To ensure that any vinyl chloride detected was in fact produced by bacterial degradation of the trichloroethylene, it was labeled with a naturally-occurring non-radioactive carbon isotope (carbon-13), and the presence of carbon-13 in the vinyl chloride produced was confirmed by mass spectrometry. Vinyl chloride formation from trichloroethylene was confirmed, after 1 and 3 weeks incubation.

Prior to testing the California landfill samples, the researchers took samples of primary sewage sludge from the anaerobic digesters at the City of Richland, Washington, wastewater treatment plant. This material represents anaerobically digested sewage that presumably has never been exposed to any form of chlorinated industrial solvent, but may contain organisms similar to those in the landfill samples. When exposed to labeled trichloroethylene under the same conditions as the landfill samples, vinyl chloride was also formed, showing that the ability of microorganisms to degrade solvents is not restricted to those found in landfills.

In both cases, vinyl chloride was formed by anaerobic dechlorination of common chlorinated solvents. Such solvents may enter landfills in items such as paints, paint thinner, plastic wrap, garden hoses, and phonograph records. Older landfills may contain more vinyl chloride, as this compound was not recognized as carcinogenic until recently, and permitted levels of the residual gas contained in PVC plastic used to be much higher than they are today. Decomposition of PVC (polyvinyl chloride)itself does not appear to contribute significantly to vinyl chloride release.

In summary, vinyl chloride emissions from landfills appear to come from household and industrial materials, by conversions by microorganisms indigenous to the landfills themselves.

Although not currently considered a health hazard, at observed levels, these emissions deserve further study and monitoring. Vinyl chloride is not persistent in the environment (50% decomposes in sunlight in 4.5 hr), but can be a cause for concern in any amount. The problem may be alleviated by minimizing the amounts of chlorinated solvents dumped into municipal landfills, by collecting and burning the evolved gases, or by more innovative techniques currently under development. This project will help provide additional information from which useful and meaningful regulatory actions can be taken.

Battelle's Pacific Northwest Division, with laboratories in Richland, Seattle, and Sequim, Washington, performs research and development for industrial sponsors and government agencies. The Division is a component of Battelle Memorial Institute, the world's largest independent research institute. Other major Battelle research facilities are located in Columbus, Ohio; Frankfurt, West Germany; and Geneva, Switzerland.

APPENDIX C: INDUCTIVELY COUPLED PLASMA (ICP) ELEMENTAL ANALYSIS PROCEDURE

Sample ignited in a platinum crucible using Na_2CO_3 as follows:

1. Place about 1g Na_2CO_3 in a platinum crucible.
2. Weigh between 0.36-0.40g sample. Place the sample in the platinum crucible. Add 1g Na_2CO_3 over the sample.
3. Place sample in a muffle furnace. Cover with a platinum lid and set temperature of muffle at 150 C and heat for 15 min.
4. Increase temp. at 50 increment for 15 min. to a temp. of 950 C.
5. Cool to room temp.
6. Leach melt with H_2O in a 300 ml beaker. Acidify with 50 ml 1:1 HCl.
7. Transfer solution into a 250 ml volumetric flask. Dilute to volume with deionized water.
8. Pipet 10 ml of solution into a 100 ml volumetric flask. Dilute to volume with deionized water.
9. Analyze the sample using an Inductively Coupled Argon Plasma/Atomic Emission Spectometer (ICP/AES).
10. Calculation:

$$\text{Wt\% element} = \frac{\text{Mg/ml element} \times 2500 \times 100}{\text{Mg sample}}$$