

PRELIMINARY ASSESSMENT OF THE ENVIRONMENTAL PROBLEMS

ASSOCIATED WITH

VINYL CHLORIDE AND POLYVINYL CHLORIDE

(Appendices)

Report on the Activities and Findings of the  
Vinyl Chloride Task Force

Environmental Protection Agency

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## SELECTED ECONOMIC CONSIDERATIONS

Production Levels

During 1973, VC production was at the 5.3 billion pound level with PVC and its copolymers at the 4.6 billion pound level. PVC has become a very important polymer as evidenced by the broad dependence of nearly every branch of industrial and commercial activity upon products and components fabricated from this plastic. In Table 1, major PVC products manufactured during 1973 are identified.

The U.S. VC/PVC industry has been operating for more than forty years, and over the past five years has shown an average annual growth rate of 14 percent -- a rate of growth that had been expected to taper off only moderately in the next few years.

The size of this industry can be appreciated by considering that the synthesis of the monomer is conducted in fifteen U.S. plants, and forty-three facilities are engaged in polymerization of PVC (including its use as a copolymer) with almost all of these plants currently operating at or near capacity. At least 7,500 plants are engaged in fabricating products from PVC. About 1,500 workers are employed in monomer synthesis and an additional 5,000 in polymerization operations. Estimates have suggested that up to 350,000 workers may be associated with the fabrication plants.

The wholesale value of the annual output of fabricated products based on PVC is at least several billion dollars.

Competitive Substitution

Should requirements for worker safety or environmental controls drive the price of PVC resin upward, it seems likely that some PVC products would be displaced by products using other plastics or other materials. Other products dependent on PVC might disappear altogether from the marketplace. Probably one-fourth to one-third of current PVC products by value are marginally competitive with other plastic products. At significantly higher prices a lesser number probably would find substitutes in other materials at higher costs. Identified in Table 2 are a few of the substitute materials that might be considered. For some uses, there are no apparent substitutes.

Table 1  
MAJOR PVC PRODUCTS

| <u>Market Category</u>        | <u>Products</u>                         | <u>1973<br/>1000 metric tons</u> |
|-------------------------------|-----------------------------------------|----------------------------------|
| I. Apparel                    | Baby pants                              | 12                               |
|                               | Footwear                                | 66                               |
|                               | Outerwear                               | 31                               |
| II. Building and Construction | Extruded foam moldings                  | 26                               |
|                               | Flooring                                | 211                              |
|                               | Lighting                                | 5                                |
|                               | Panels and siding                       | 39                               |
|                               | Pipe and conduit                        | 525                              |
|                               | Pipe fittings                           | 44                               |
|                               | Rainwater systems, soffits, facias      | 16                               |
|                               | Swimming pool liners                    | 18                               |
|                               | Weatherstripping                        | 16                               |
|                               | Windows                                 | 26                               |
| III. Electrical               | Wire and cable                          | 194                              |
| IV. Home                      | Appliances                              | 20                               |
|                               | Furniture                               | 145                              |
|                               | Garden hose                             | 18                               |
|                               | Housewares                              | 51                               |
|                               | Wall coverings and wood surfacing films | 54                               |
| V. Packaging                  | Blow molded bottles                     | 36                               |
|                               | Closure liners and gaskets              | 9                                |
|                               | Coatings                                | 9                                |
|                               | Film                                    | 59                               |
|                               | Sheet                                   | 35                               |
| VI. Recreation                | Phonograph records                      | 66                               |
|                               | Sporting goods                          | 25                               |
|                               | Toys                                    | 88                               |
| VII. Transportation           | Auto mats                               | 18                               |
|                               | Auto tops                               | 15                               |
|                               | Upholstery and seat covers              | 83                               |
| VIII. Miscellaneous           | Agriculture (incl. pipe)                | 66                               |
|                               | Credit cards                            | 8                                |
|                               | Laminates                               | 23                               |
|                               | Medical tubing                          | 23                               |
|                               | Novelties                               | 7                                |
|                               | Stationery supplies                     | 18                               |
|                               | Tools and hardware                      | 8                                |
|                               | Other                                   | 45                               |
|                               | Total                                   | 2158                             |

Table 2  
SUBSTITUTE MATERIALS FOR PVC PRODUCTS

| <u>PVC PRODUCT</u>    | <u>SUBSTITUTES</u>      | <u>SAME PRICE RANGE</u> | <u>HIGHER PRICE</u> |
|-----------------------|-------------------------|-------------------------|---------------------|
| Pipe & Tubing         | Polyethylene            | X                       |                     |
|                       | Polypropylene           | X                       |                     |
|                       | Metals                  |                         | X                   |
|                       | ABS resins              |                         | X                   |
| Flooring              | Asphalt                 | X                       |                     |
|                       | Wood                    |                         | X                   |
|                       | ABS resins              |                         | X                   |
| Electrical Insulation | Polyethylene            | X                       |                     |
|                       | Polypropylene           | X                       |                     |
|                       | EPDM rubbers            |                         | X                   |
|                       | SBR rubbers             |                         | X                   |
|                       | TFE plastics            |                         | X                   |
| Records               | ABS resins              |                         | X                   |
|                       | Acrylics                |                         | X                   |
| Film & Sheet Products | Polyvinylidene chloride |                         | X                   |
|                       | Polyethylene            | X                       |                     |
|                       | Polypropylene           | X                       |                     |
|                       | Cellulosics             |                         | X                   |
| Coatings              | Acrylics                |                         | X                   |
|                       | Polyurethanes           |                         | X                   |
|                       | Cellulosics             |                         | X                   |
| Household Goods       | Styrene                 | X                       |                     |
|                       | Polyethylene            | X                       |                     |
|                       | Polypropylene           | X                       |                     |
|                       | Wood                    |                         | X                   |
|                       | Metals                  |                         | X                   |
|                       | Acrylics                |                         | X                   |
| Packaging             | Polyethylene            | X                       |                     |
|                       | Polypropylene           | X                       |                     |
|                       | Polyvinylidene chloride |                         | X                   |
|                       | Cellulosics             |                         | X                   |
|                       | Acrylics                |                         | X                   |
|                       | Polyurethanes           |                         | X                   |
|                       | Glass                   |                         | X                   |

## International Aspects

U. S. based manufacturers currently produce about one-third of the western world's supply of resins, with the U. S. market also consuming about one-third of the total. In 1973, 3.7 percent of PVC and 7.8 percent of VC manufactured in the United States were exported. Prior to the recent U. S. concern over worker and environmental controls at VC and PVC facilities, there was no reason to anticipate a major change in the U. S. share of production or market during the next few years. Recent increases in demand for PVC resins -- and concurrently for VC -- at attractive prices have been of worldwide dimensions with expansion plans for PVC manufacturing being considered by a number of companies at home and abroad.

There is presently an import duty on PVC resin from countries with status as Most Favored Nations of 1 1/4 cents per pound plus six percent ad valorem and from other nations of four cents per pound plus 30 percent ad valorem. Given the current U. S. market price of 18 to 24 cents per pound for the general purpose uncompounded resin, there has been little incentive to import PVC resin. Also, there currently is little export incentive because of short U. S. supply and unattractive foreign prices. However, higher prices as a result of more stringent worker or environmental controls in PVC resin plants in the United States than abroad might well stimulate significantly increased imports.

## Control Technology

While there appear to be a number of general approaches for reducing the discharge of VC into the environment at VC and PVC resin plants and the discharge of PVC at resin plants, in many respects the approaches must be tailored to the individual plants. All VC plants and some PVC resin plants are outdoors while other PVC plants are at least partially enclosed. A variety of production processes are used, and different kinds of technology are employed. However, there are some common measures that would reduce VC emissions.

### FOR VC PLANTS:

1. Reducing the escape into the atmosphere of VC when venting the tank car gauge tube, disconnecting the feeding line, and closing the valves during rail tank car loading. Mechanical disconnect devices and double block and bleed piping are available to ease this problem.
2. Improving the quality of pumps to reduce the possibility of leakage due to failure of seals. Pumps are available today which could minimize this problem.
3. Venting unintentional leaks and spills into a system which is flared and, preferably, scrubbed.

#### FOR PVC RESIN PLANTS:

1. Collection and destruction of purge gases from the reaction kettles prior to opening for cleaning, sampling, or recharging.
2. Centralized collection and filtering of VC vapor discharges from dryers and centrifuges.

With regard to PVC particulate in air and water discharges, improved housekeeping and relatively simple ventilation filtering systems are usually technically feasible and effective.

Laboratory data have shown that VC can be adsorbed on activated carbon. Concentrated VC vapor streams have produced a recovery working capacity on carbon equivalent to about ten percent of the carbon weight. Ambient air contaminated with low levels of VC produces significantly lower adsorbent working capacities. Control of dilute VC is therefore possible but may not be practical using activated carbon. Carbon regeneration using steam or pressure swing appears possible, with recovery of desorbed VC for recycle.

Clearly, these approaches will not eliminate losses but should materially reduce them. In the longer run, the development of continuous flow processes, the use of larger kettles, better housekeeping, and/or reductions in the number of feed lines might result in more dramatic reductions of VC leakage.

#### REFERENCES

1. Modern Plastics, Jan 1974, p. 43
2. The 1972 Census of Manufacturers shows 7,574 plants manufacturing miscellaneous plastics products (SIC 3079), a substantial number of which use PVC. SIC 3079 probably covers most, but not all, PVC fabricators.
3. Discussions with representatives of the Department of Commerce, Manufacturing Chemists Association, and Society of Plastics Industry.

## PRODUCERS OF VINYL CHLORIDE AND POLYVINYL CHLORIDE

The major producers of VC, PVC, and PVC copolymers are listed in this section with the plant location and available capacity data.

VC Producers

|                                | <u>Location</u>    | <u>Annual Capacity<br/>(Millions of Pounds)</u> |
|--------------------------------|--------------------|-------------------------------------------------|
| Allied Chemical Corporation    | Baton Rouge, La.   | 300                                             |
| American Chemical Corporation  | Long Beach, Calif. | 175                                             |
| Continental Oil Company        | Westlake, La.      | 650                                             |
| Dow Chemical, U.S.A.           | Freeport, Tex.     | 200                                             |
|                                | Oyster Creek, Tex. | 700                                             |
|                                | Plaquemine, La.    | 390                                             |
| Ethyl Corporation              | Baton Rouge, La.   | 300                                             |
|                                | Pasadena, Tex.     | 150                                             |
| B.F. Goodrich Chemical Company | Calvert City, Ky.  | 1000                                            |
| Monochem, Inc.                 | Geismar, La.       | 300                                             |
| PPG Industries, Inc.           | Lake Charles, La.  | 400                                             |
|                                | Guayanilla, P.R.   | 500                                             |
| Shell Chemical Company         | Deer Park, Tex.    | 840                                             |
|                                | Norco, Tex.        | 700                                             |
| Tenneco, Inc.                  | Houston, Tex.      | 225                                             |

PVC Producers

|                                  |                      |     |
|----------------------------------|----------------------|-----|
| Air Products and Chemicals, Inc. | Calvert City, Ky.    | 150 |
|                                  | Pensacola, Fla.      | 50  |
| American Chemical Corporation    | Long Beach, Calif.   | 150 |
| Borden, Inc.                     | Illioopolis, Ill.    | 140 |
|                                  | Leominster, Mass.    | 180 |
| Continental Oil Company          | Aberdeen, Miss.      | 235 |
|                                  | Oklahoma City, Okla. | 240 |

| <u>Company</u>                         | <u>Locations</u>         | <u>Annual Capacity</u><br>(Millions of Pounds) |
|----------------------------------------|--------------------------|------------------------------------------------|
| Diamond Shamrock Chemical Company      | Deer Park, Tex.          | 270                                            |
|                                        | Delaware City, Del.      | 100                                            |
| Ethyl Corporation                      | Baton Rouge, La.         | 180                                            |
| The Firestone Tire & Rubber Company    | Perryville, Md.          | 230                                            |
|                                        | Pottstown, Pa.           | 270                                            |
| The General Tire & Rubber Company      | Ashtabula, Ohio          | 125                                            |
|                                        | Pleasants County, W. Va. | 50                                             |
| B. F. Goodrich Chemical Company        | Avon Lake, Ohio          | 140                                            |
|                                        | Henry, Ill.              | 140                                            |
|                                        | Long Beach, Calif.       | 140                                            |
|                                        | Louisville, Ky.          | 340                                            |
|                                        | Pedricktown, N.J.        | 170                                            |
| The Goodyear Tire & Rubber Company     | Niagara Falls, N.Y.      | 100                                            |
|                                        | Plaquemine, La.          | 100                                            |
| Great American Chemical Corporation    | Fitchburg, Mass.         | 40                                             |
| Hooker Chemical Corporation            | Burlington, N.J.         | 180                                            |
|                                        | Hicksville, N.Y.         | 15                                             |
| Keysor-Century Corporation             | Saugus, Calif.           | 35                                             |
|                                        | Delaware City, Del.      | 35                                             |
| Monsanto Company                       | Springfield, Mass.       | 70                                             |
| National Starch & Chemical Corporation | Meredosia, Ill.          | 10                                             |
| Olin Corporation                       | Assonet, Mass.           | 150                                            |
| The Pantasote Co. of New York, Inc.    | Passiac, N.J.            | 60                                             |
|                                        | Point Pleasant, W. Va.   | 90                                             |
| Robintech, Inc.                        | Painesville, Ohio        | 250                                            |
| Stauffer Chemical Company              | Delaware City, Del.      | 175                                            |
| Tenneco Chemicals, Inc.                | Burlington, N.J.         | 165                                            |
|                                        | Flemington, N.J.         | 70                                             |
| Union Carbide Corporation              | South Charleston, W. Va. | 160                                            |
|                                        | Texas City, Tex.         | 240                                            |
| Uniroyal, Inc.                         | Painesville, Ohio        | 140                                            |

# PVC Copolymer I

## Company

### A. Polyvinyl

Air Products and C

### B. Polyvinyl Cl

Air Products and C

American Chemical

Atlantic Tubing & R

Borden, Inc.

The Firestone Tire

B.F. Goodrich Chem

Hooker Chemical C

Keysor-Century Co

National Starch and

Olin Corporation

The Pantasote Com

### C. Polyvinyl Cl

BASF Wyandotte C

Borden, Inc.

### mer Re

### polymer

Compan

sany

Corporation

w York, Inc.

### ylidene Chloride Copc

## Locat

Calve.

as

Calvert C

Long Beach, Calif.

Cranston, R.I.

Bainbridge, N.Y.

Compton, Calif.

Demopolis, Ala.

Illiopolis, Ill.

Leominster, Mass.

Pottstown, Pa.

Avon Lake, Ohio

Louisville, Ky.

Hicksville, N.Y.

Saugus, Calif.

Meredosia, Ill.

Assonet, Mass.

Passaic, N.J.

Point Pleasant, W.Va.

### Resins

South Kearny, N.J.

Bainbridge, N.Y.

Compton, Calif.

Demopolis, Ala.

Illiopolis, Ill.

Leominster, Mass.

Dow Chemical, U.S.A.

B.F. Goodrich Chemical Company

W.R. Grace & Company

Morton-Norwich Products, Inc.

National Starch and Chemical Corporation

SCM Corporation

Tenneco, Inc.

Union Carbide Corporation

Midland, Mich.

Louisville, Ky.

Owensboro, Ky.  
South Acton, Mass.

Ringwood, Ill.

Meredosia, Ill.

Huron, Ohio

Burlington, N.J.  
Flemington, N.J.

Institute and South  
Charleston, W. Va.  
Texas City, Texas

#### REFERENCES

1. 1974 Directory of Chemical Producers, USA, - Chemical Information Services, Stanford Research Institute, Menlo Park, California, 1974.
2. Chemical Marketing Reporter, May 20, 1974.

## THE MATERIALS BALANCE AT VINYL CHLORIDE AND POLYVINYL CHLORIDE FACILITIES

### Vinyl Chloride Production Facilities

Detailed, reliable data for estimating material losses at VC facilities with precision are not readily available. Therefore, only generalized estimates have been attempted.

A simplified block diagram for production of VC from ethylene and chlorine is shown in Figure 1. Some VC complexes utilize oxychlorination units; others produce ethyl chloride from the by-product hydrogen chloride (HCl) and ethylene. However, the production of dichloroethane (EDC) allows for many approaches to recycling of light and heavy materials such that the losses of VC are reduced. Even vent streams of inerts can be scrubbed with EDC for maximum removal of VC before venting. Light ends such as methane are usually flared and VC is converted to water and small amounts of HCl.

VC losses have come primarily from vent streams, the storage and transportation loading systems, and seepages from pumps. If vent streams are not scrubbed or flared, the amount of VC reaching the atmosphere increases considerably. This in turn is influenced by the purity of the ethylene and the chlorine being fed into the units. Usually, these inerts come out in the EDC unit but may be carried on depending upon the producer's philosophy regarding the purity of the EDC to be fed to the cracker. Experience has been that the higher the purity of EDC both with regard to light and heavy material, the greater the efficiency of the cracking.

It is frequently difficult to pinpoint the areas and quantities of VC losses. However, some generalizations can be made for, as an example, a plant producing 500 million pounds per year of VC. (The industry is heading toward plants of this size and larger.) Tank car loading losses may be several hundred pounds per day. Vent stream losses could reach another 100 pounds per day while losses of VC entrapped in the water effluent might be a few pounds per day. In addition to these very small operating losses, there are undoubtedly unintentional losses from leaking pumps, flanges, and containment vessels, with total plant losses probably less than 0.1% or less than 500,000 pounds per year.

From an environmental standpoint, the disposal of the heavy chlorinated hydrocarbons may also present a problem. Some are sold to solvent scrap dealers for salvage. In the past much of the material has been dumped at sea or put into landfills or deep wells. More recently, incineration has been used, which is known to produce HCl emissions.

## Polyvinyl Chloride Polymerization Facilities

Reasonably reliable data are available for estimating material losses at PVC facilities. However, generalizations applicable to the entire industry must be surrounded with many caveats. It must be emphasized that there are a number of PVC processes, and each plant has its own idiosyncrasies.

VC losses will fluctuate depending on the care exercised in operating the PVC plant, types of products produced, frequency of product change, method of PVC shipment, and emergency situations. Estimates of losses have varied widely in the industry, indicating the complexity of establishing precise losses for a given facility and overall losses on a nationwide basis.

In general, older PVC plants are smaller than those being built today and are equipped with smaller sized reactors. With small reactors, the number of batches required to produce a given amount of PVC is greater, and thus the number of process steps are increased with a greater potential for loss of both VC and PVC. Further, a small plant has the disadvantage of having to make frequent resin changes to meet customer demands. During these changeovers a certain amount of off-grade resin is produced.

In addition, older plants have the added burden of higher maintenance than new plants, but this tends to stabilize after a few years. The handling of VC and the production of the high quality resins which are demanded by the marketplace require a reasonable maintenance program. Maintenance consists primarily of the care of agitator seals, pump seals, and valves and the removal of polymer which slowly builds up in VC lines -- primarily in the recovery system. Although many older facilities have been in operation for years, they are usually not the same as when first installed. Some of the operators have continually updated the plants for many reasons including labor savings systems, new product requirements, replacement of wornout equipment, addition of new product lines, and safety.

When VC was cheap and there was little concern about its toxicity, the emphasis was almost exclusively on productivity. Often this resulted in high losses of VC to the environment as recovery cycles were reduced. Today, the picture is changing. Not only are the producers trying to reduce the direct VC losses, but they are also trying to minimize PVC losses by scheduling longer production runs between product changes. As an example, the newer large plants are setup with multiple production lines. This allows the dedication of one line to a given product which results in very low resin loss due to product change.

The traditional method of stating yield of VC in PVC plants has been based upon pounds of prime resin in the bag as compared to VC invoiced. This often has led to a misunderstanding about VC losses with the interpretation that a 94% yield means 6% VC loss to the environment. In fact some VC may never actually be received because of the inability to measure the weight of tank cars accurately, some of the losses are in the form of PVC scrap, and some losses escape as PVC particles.

A properly run and maintained suspension plant using technology that is ten years old should be capable of obtaining a 95% or higher yield unless some especially esoteric resin is being produced along with large amounts of scrap or off-grade resin. For the older plants, the losses will probably be significantly higher. Other than overall sloppy operation, the recovery system is the single most important part of the plant governing VC losses. If insufficient time is allowed or vacuum is not applied, then the VC content in the PVC/water slurry will be greater than necessary. As a result, VC losses will occur in the centrifuge effluent water, drier/ product collector vent air, the venting of the reactor, and the slurry tank.

The magnitude of VC and PVC losses in a typical PVC plant is described in Figure 2. These losses are expressed as a range of losses depending on the feed rate, reactor size, reactor cleaning procedures, batch sizes, level of technology, and general housekeeping and operating procedures.

The following comments on manufacturing practices may help put these losses into perspective:

1. VC Feed - This is shipped as virtually 100% VC and does not normally contain an inhibitor.

2. VC Unloading - Considering normal losses in disconnecting the piping, sampling, tank gauging, pump and compressor seals to the tank cars, losses to the atmosphere should not be greater than 100 pounds per car.

3. VC Charging - A 0.05% loss between storage and polymerization should cover losses from flanges and seals throughout all VC handling equipment.

4. Polymerization - The loss from build-up of PVC on the walls of the reactor is split between reactor wash-out and the slurry strainer.

5. Reactor Venting - Before the reactor can be cleaned, residual VC is vented. After recovery and emptying the PVC resin, the reactor is full of a mixture of air, moisture, and VC at ambient conditions.

6. Recovery - Processing schemes will vary, but one of the most widely used is the direct recovery of unreacted VC from the reactor. While the reaction can be carried out further, economically it is essentially complete at 90% conversion or even less depending on the type of resin. At this point the residual VC is recovered by means of compressors which evacuate VC from the reactor. The recovered VC is condensed and distilled before recycling to the reactor.

7. Drying - Unreacted VC is collected in the recovery system but there are losses of polymer in the drier due to coalescence of the resin and periodic clean-out. This is almost entirely scrap.

8. Product Collector - Most plants use bag collectors so that the loss of resin is less than one pound per hour, but there are losses due to product changes which raise the total.

9. Screening - Oversize resin is removed from the final product. This material consists of scrap and off-grade resin. With the current PVC shortage much of this off-grade resin is used as prime resin by special customers.

10. Miscellaneous - In addition to the above losses, others occur as scrap or off-grade polymer and as quality control samples.

- a. Bad Batches - Most plants experience batches which are off specification. These range from "just slightly off" to solid batches, with losses at 2 to 3 batches per month or about 0.4% or 40 pounds per hour average. Salvage value depends upon the degree of "off-grade" and market conditions.
- b. Samples - Probably about 0.05% or 5 pounds per hour and is usually destroyed in testing.
- c. Polymer Build-up - VC slowly polymerizes in the pipe lines, particularly the recovery system, and must be removed periodically. No quantitative value is available for this loss.
- d. Spillage - Some of the product is shipped in bulk and some is bagged. While some spillage occurs in bulk handling, more occurs in bag filling and in bag breakage.
- e. Centrifuge Effluent - Some PVC enters the effluent water.

11. Product Change-Over - As indicated previously there are losses in the drier and collector due to cleaning for changes from one product to another. In addition one must segregate the first product that comes through this system. The amount can vary widely depending upon the number of changes and the sensitivity of the product to contamination from the previous product.

The foregoing analysis, together with estimates provided by industry, suggests that the losses of VC at PVC polymerization facilities currently range from about 3.0 to 6.3% while PVC losses are on the order of 1.3%.

PRODUCTION OF VC FROM ETHYLENE AND CHLORINE  
SIMPLIFIED BLOCK DIAGRAM

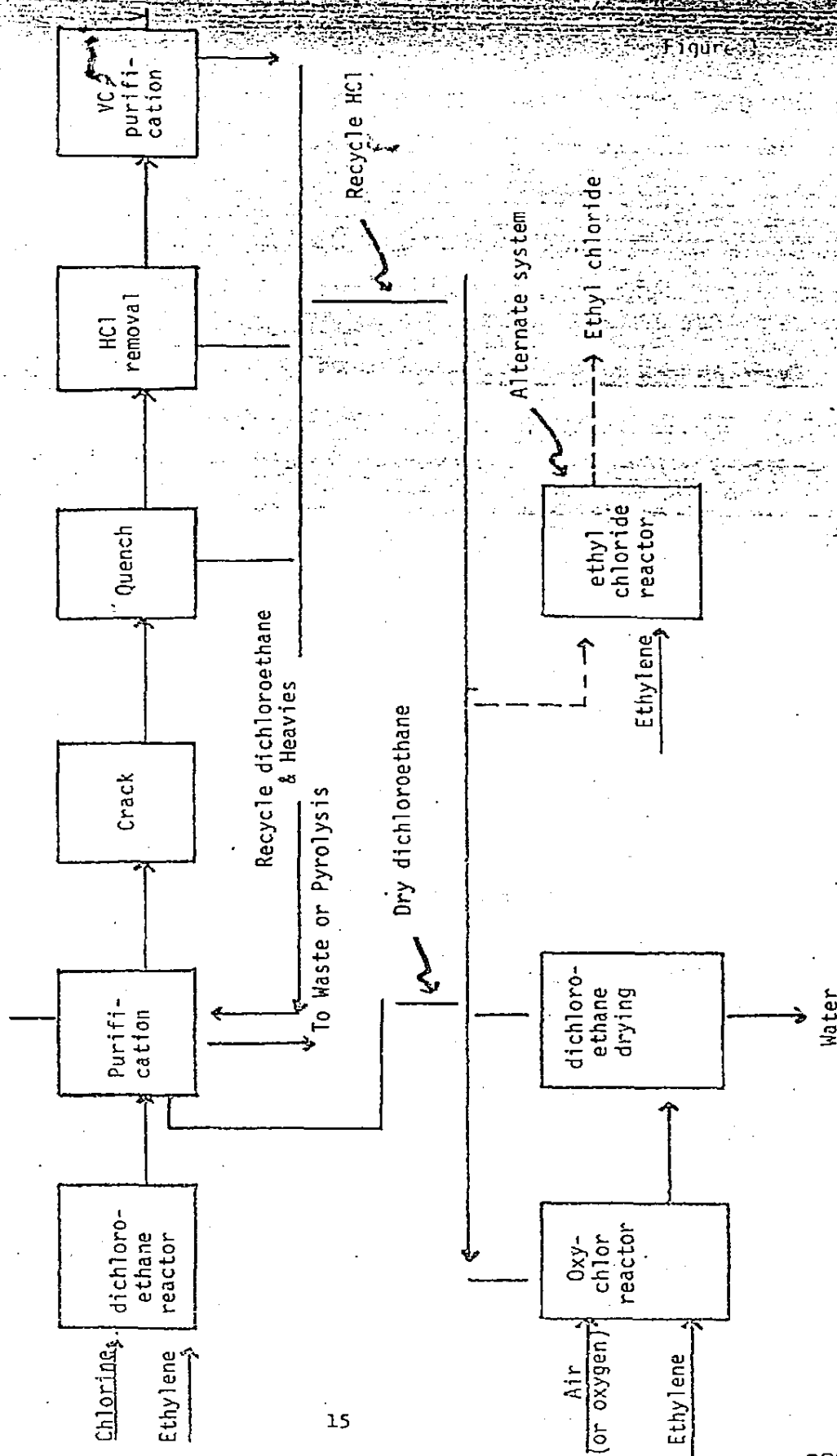
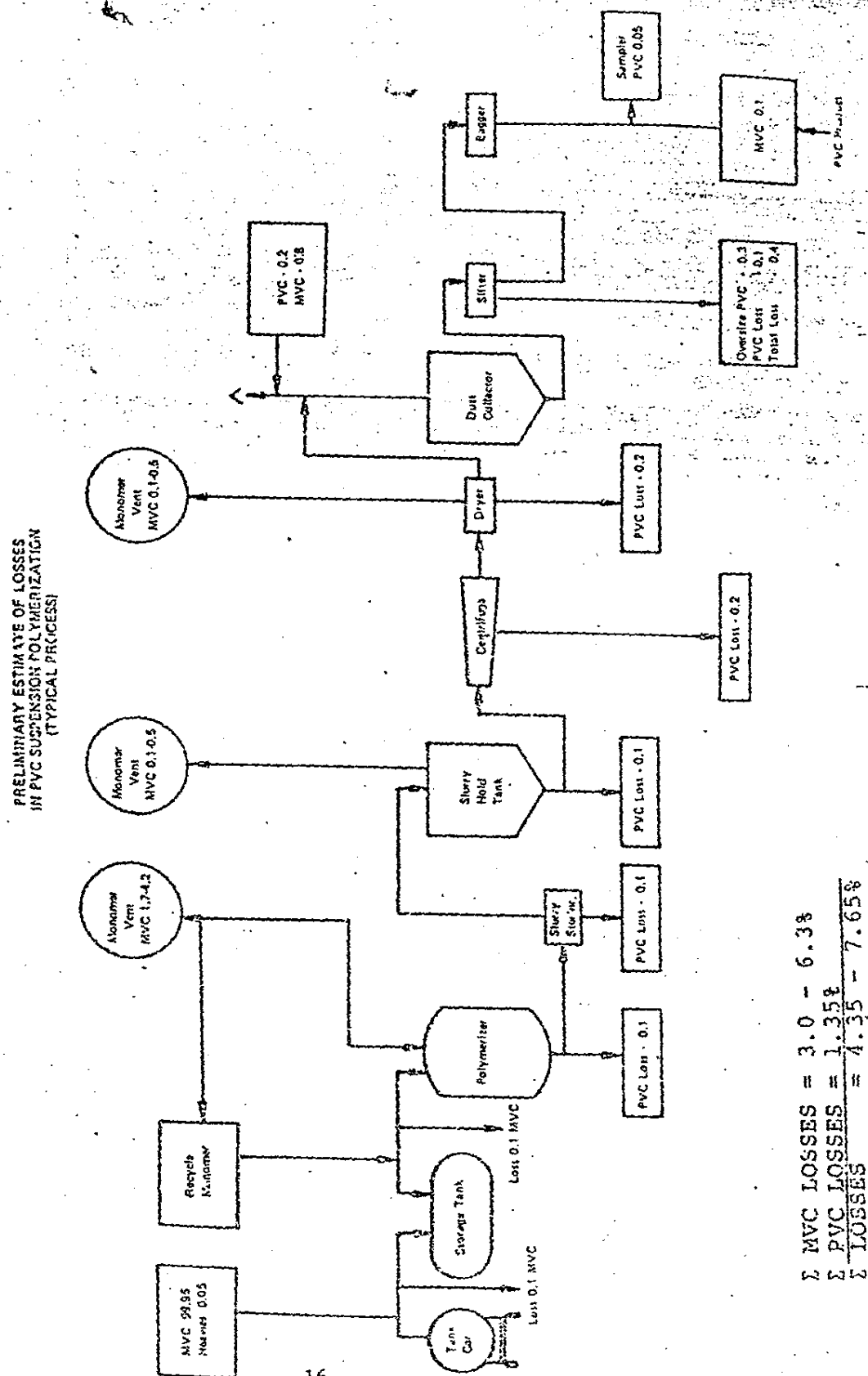


Figure 2



Σ MVC LOSSES = 3.0 - 6.3%

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Σ PVC LOSSES = 1.35%

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Σ LOSSES = 4.35 - 7.65%

## INTERIM METHOD FOR SAMPLING AND ANALYSIS OF VINYL CHLORIDE IN WASTE WATER EFFLUENTS AND AIR EMISSIONS

### Scope and Application

The initial basis for this method was developed during the monitoring program carried out by EPA Region IV in March and April. The techniques used by Region IV provided guidance for the monitoring activities of other Regions, and the experiences of all Regions were then incorporated into this refined version of the original Region IV approach.

This method is applicable to VC determinations in water effluents, sludges and scums, and atmospheric emissions. The limit of detection is approximately 0.06 mg/l in water and 0.06 ppm (v/v) in air samples.

### Summary of Analytical Procedures

Water composite samples, air continuous composite bag samples, and air and water grab samples are analyzed without cleanup by gas chromatography (GC). Separations are effected by selection of one of two types of columns depending upon the nature of the sample. Detection is by means of the flame ionization detector (FID). Tetrahydrofuran extracts of sludges and scums are used for injection into the GC. Air continuous samples on activated carbon are extracted with carbon disulfide, and the extract is analyzed by direct injection into the GC.

Calibration curves are developed using gravimetrically prepared calibration solutions, or by using known dilutions of VC in carrier gas.

VC confirmation should be made by mass spectrometric analysis of the GC eluent if possible. Independent confirmation may also be made in the event of extraordinarily high VC concentration samples by using long path Fourier transform IR spectrophotometry. This IR technique requires special equipment and about 20 cubic feet of air samples.

### Interferences

Certain volatile hydrocarbons such as neopentane, butadiene, and freon 12 have elution characteristics similar to VC. However, on the GC column substrates specified in these procedures, these have not usually presented problems of resolution of the VC peak. When column substrates other than those specified have been used, impurities from solvents and carbon adsorbents have been

found to interfere with the VC elution peak. Under certain conditions a peak is associated with the injection and subsequent withdrawal of the microsyringe into and from the GC septum. These peaks can also give interferences with the VC peak. Withdrawal should be timed to avoid overlap of this peak with the VC peak.

#### Apparatus and Materials

##### Gas Chromatograph

##### Flame Ionization Detector

Recorder - any potentiometric strip chart recorder which is compatible with the detector system. An integrator is also desirable to estimate peak areas.

##### Column Materials for Waste Water, Sludge, or Scum Samples

Borosilicate glass tube or stainless steel tube - 6' x 2.5 mm ID preferred. When GC configuration requires columns of other dimensions, these should be used.

Solid support - 60 to 80 mesh Gas Chrom Q

Liquid Phase - 4% FFAP on specified solid support (weight percent). Liquid phase on solid support can be purchased directly from commercial distributors.

##### Column Materials for Air Samples

Borosilicate glass tubing or stainless steel tubing - 8' x 2.5 mm ID preferred. When GC configuration requires columns of other dimensions, these should be used.

Solid support - Carbopak A

Liquid phase - 0.4% Carbowax 1500 on solid support (weight percent). Liquid support on solid phase can be purchased directly from commercial distributors.

##### Continuous Air Monitoring Materials - Carbon Adsorption Option

Adsorption Tube - pyrex glass, 18" x 3/8" OD

Activated coconut charcoal, 8-16 mesh. Any good commercial grade, e.g. Fischer Scientific Company can be used.

Becton-Dickson 27 gage 3/8" hypodermic needle flow control

Vacuum pump

Air flow meter

Continuous Air Monitoring Materials and Equipment - Bag Sampling Option

Environmental Measurements, Inc., Programmable Bag Sampler

Tedlar bags (or equivalent)

Gas Pressure Regulator (0-5 PSIG)

Microsyringes - 10, 25, 50, and 100 microliter (graduated)

Gas-tight sample syringes - 1 and 50 ml (graduated)

Vacuum Sampling Cans - 370 ml steel Vacu-Samplers, or glass sampling bottles. Cans and bottles should be flushed with clean air or nitrogen and evacuated prior to use. Evacuated containers should be protected from rough handling to prevent implosion or collapse.

Sampling Bags (Tedlar or equivalent) - 12" x 12", 36" x 36", equipped with sampling valves and speta for GC sample withdrawal

Automatic water sampler - compositor (manual sampling is optional) equipped with sample refrigeration capabilities, and a means to prevent loss of vinyl chloride from open bottles

Glass sampling bottles with teflon lined screw type caps - 50 ml capacity or other sizes depending upon sampler requirements

Septum-sealed vials - 1 to 10 ml capacity

Volumetric Flask, Glass stoppered, 25 ml

Medicine droppers

Dedicated GC/M.S. for confirmatory tests (preferable)

Barometer

Thermometer

Anemometer

Reagents, Solvents, and Standards

Carrier gases - zero nitrogen or helium

FID gases - zero hydrogen, oxygen

Tetrahydrofuran, reagent grade, peroxide-free

Carbon tetrachloride (reagent grade)

Carbon disulfide (reagent grade)

Standards

VC in zero air, 50 ppm ( $\pm 2\%$ ) v/v

VC, analyzed reagent grade (lecture bottle)

### Sampling

#### A. Water Samples

All waste water discharge points identified in NPDES permits should be sampled for VC. A minimum of three successive 24-hour composite samples of each site should be taken. Compositing interval should be one hour (manual or automatic sampling is optional). Compositing interval of 20 minutes may be used if the automatic sampler has this capability. Samples should be taken at waste treatment units such as clarifiers and scum and sludge separators. Two 8-hour composites should be taken from the effluents from each of these points, and one 8-hour composite should be taken of scum and sludge from each separator unit.

Compositing interval should be one hour. Three grab samples of clean process water (city or private well) should be taken as blanks.

Samples should be taken in 50 ml bottles with gas-tight, teflon-sealed, screw cap closures, or in equivalent containers required by the characteristics of automatic samplers. All water, sludge, and scum samples should be refrigerated during collection and storage. Compositing volumes should be selected to assure head space above the sample is absent or minimized to avoid loss of VC by its partitioning into the gas phase when samples are sealed. Provisions should be made to avoid such losses during continuous monitoring operations.

Estimates of discharge flows should be made using any appropriate measuring device (venturi, weir, magnetic meter, etc.).

Samples should be preserved by refrigeration and protected from sunlight until they are ready for analysis.

#### B. Air Samples

Sampling sites should be selected which are downwind and in the plume of the atmospheric emissions from the plant. Samples should be collected only in areas where local residents or neighboring industries would be exposed. At a minimum,

sampling should be conducted over a period of five days. Sites should be selected in the following array: one site immediately upwind (A) and one immediately downwind (B) of the plant site; four sites about 0.4 miles from the plant site, one laterally left (C) and one laterally right (D) of the plant site on a line roughly perpendicular to the prevailing wind direction and two (E, F) downwind from the plant site; two sampling sites (G, H) approximately 0.5 miles downwind; single sampling sites, each at distances approximately 0.6 (I), 0.8 (J), 1.0 (K), and 3.0 (L) miles downwind from the plant site. If wind is fish-tailing severely, move sampling sites G and H approximately 0.5 mile upwind of the fish-tailing wind direction from the plant. The sites specified are minimum. Additional sites may be selected contingent on overriding micrometeorological considerations. These should be determined in consultation with the Regional meteorologist. These may be at ground or some elevated level, as determined by the plume survey or as estimated by release of meteorological balloons, anemometer, and wind direction indicators, etc.

#### SAMPLING SITES

| <u>Prevailing Wind Direction</u> |                    | <u>Minimum Sampling Schedule</u> |                                                                                                                      |            |            |            |
|----------------------------------|--------------------|----------------------------------|----------------------------------------------------------------------------------------------------------------------|------------|------------|------------|
| <u>Miles from plant site</u>     | <u>Site Symbol</u> |                                  | <u>Time</u>                                                                                                          | <u>Mon</u> | <u>Wed</u> | <u>Fri</u> |
| 0.0                              |                    | A                                |                                                                                                                      |            |            |            |
| 0.4                              | C                  | <u>Plant</u>                     | 0800                                                                                                                 | A, A, B    | A, B, B    | A, A, B    |
| 0.0                              |                    | B                                | 1000                                                                                                                 | C, D, F    | C, D       | C, D, D    |
| 0.4                              |                    | E F                              | 1200                                                                                                                 | A, E       | A, G, G    | A, E       |
| 0.5                              | G                  | H                                | 1400                                                                                                                 | B, B, F    | B, H       | B, B, G    |
| 0.6                              |                    | I                                | 1600                                                                                                                 | C, G       | E, K       | I, J       |
| 0.8                              | J                  |                                  | 1800                                                                                                                 | D, I       | -          | L, L       |
| 1.0                              |                    | K                                | 2000                                                                                                                 | -          | H, L, L    | -          |
| 3.0                              |                    | L                                | (Note: All times are + 30 minutes for manual grab samples, or + 2 minutes for automatic, programmable bag samplers). |            |            |            |

Grab samples should be taken in 50 ml gas-tight syringes, 50 to 100 ml glass sampling bottles, 370 ml "Vacu-Sampler" metal cans, or 12" x 12" capacity Tedlar-type bags. Both the Vacu-Samplers and the glass sampling bottles should be evacuated prior to use. (Caution: These may implode or collapse when under vacuum. Use due care in their handling). The perfect gas laws should be assumed to estimate gas volumes. Gas-tight syringes are flushed several times with ambient air before a sample is taken. After the sample is taken, the gas-tight syringe is locked and sealed until it is ready for analysis.

The Tedlar-type bag samplers may be filled by pulling the walls of the bag apart manually, or better, by placing the bag in an enclosure and pulling a vacuum on the outside surfaces of the bag. The bag is sealed until it is ready to be analyzed. Tedlar-type bags are preferred for grab sampling.

All samples should be protected from sunlight.

#### Continuous Sampling - Carbon Adsorption Option:

Continuous samples are taken in pyrex tubes (approximately 3/8" O.D. x 18" long) packed with a good grade of activated coconut shell charcoal. The charcoal is added to the tube in three segments, each 3-inches long, and each separated by a glass wool plug. The two ends of the tube are also plugged with glass wool. Both ends of the pack adsorption tube are plugged with serum caps during transport and for storage purposes.

Flow rate through the tube is controlled by inserting a Becton-Dickson 27 gage, 3/8" hypodermic needle through one of the serum caps into the end glass wool plug. Air is sucked through the tube by connecting it to a conventional vacuum pump. The arrangement is similar to that used in the National Air Surveillance Network. Flow rate should be about 200 ml per minute. For each adsorption tube, the flow rate should be calibrated in the laboratory before the sample is taken and should be verified again in the laboratory after the sample is taken. Clean needles frequently to prevent plugging.

The adsorption efficiency of the carbon in the adsorption tube should be verified in the laboratory by preparing a 5 ppm v/v VC mixture in the 36" x 36" Tedlar-type bag and drawing this through the adsorption tube. Flow rates should be verified before and after the experiment. It is important to note that all collections should be made with the adsorption tubes held in an upright position to minimize channeling. Adsorption tubes should be protected from sunlight either by wrapping with foil or by enclosing them in a box.

Each segment of the adsorption tube is worked up separately by etching the tube in the middle of a 3" section with a file, successively breaking each segment and spilling its contents into measured volumes of carbon disulfide in glass stoppered test tubes. The additions should be effected cautiously and with cooling in an ice bath since the interaction of activated carbon with carbon disulfide is quite exothermic. A 2 microliter aliquot of the supernatant solution should be injected on the carbowax 1500 column for estimation of the adsorbed VC. Successive analysis of the three adsorption tube segments will indicate the amount of break-through of VC through the adsorbent.

The same procedure should be used for taking samples in the field.

Continuous Sampling - Programmable Bag Sampler Option: The sampler is programmed to take twenty-four consecutive one-hour composite samples. Each one-hour sample is analyzed separately for VC content. Sampling rate of the individual pumps should be verified before and after use of the sampling device. Record the temperature and atmospheric pressure at which the samples are taken. All gas volumes and concentrations should be corrected to 25°C and one atmosphere (760 mm Hg). At a minimum, continuous samples should be taken at sites A, B, C, and D at ground level, unless otherwise indicated by micrometeorological conditions.

### Calibration

#### A. Gas Analysis - Gas Dilution Option:

Record ambient temperature and atmospheric pressure.

Evaluate the 36" x 36" Tedlar-type bag. Add 1 liter of the standard VC gas mixture (50 ppm, v/v) to the bag. This addition may be made with a flow meter or with a gas-tight syringe. Dilute with nine liters of zero nitrogen or helium carrier gas. This gives a concentration of 5.0 ppm (v/v) of VC. (13 ng/ml at 25°C and one atmosphere.)

Evacuate a 12" x 12" Tedlar-type bag and add 0.5 l of the 5.0 ppm (v/v) concentration mixture. Dilute with 2 liters of zero nitrogen or helium carrier gas. This gives a concentration of 1.0 ppm (v/v) VC. (2.6 ng/ml at 25°C and one atmosphere).

Evacuate a 12" x 12" Tedlar-type bag and add 0.5 l of the 1.0 ppm (v/v) VC calibration mixture. Dilute with 2 liters of zero nitrogen or helium carrier gas. This gives a concentration of 0.2 ppm (v/v) VC (about 0.52 ng/ml at 25°C and one atmosphere).

Evacuate a 12" x 12" Tedlar-type bag and add 0.75 l of the 0.2 ppm (v/v) VC calibration mixture. Dilute with 1.75 liters of zero nitrogen or helium carrier gas. This gives a concentration of 0.06 ppm (v/v) VC (about 0.16 ng/ml at 25°C and one atmosphere). This is about the limit of detection for direct injection into the GC.

With a gas-tight syringe, inject 1 ml aliquots of the 5.0, 1.0, 0.20 and 0.06 ppm (v/v) VC calibration mixtures into a GC equipped with a Carbowax 1500 or Carbowax column and an FID detector. Use zero nitrogen or helium as carrier gas at a flow rate of 60 ml/min. Operate the inlet and the column isothermally at room temperature.

Prepare a calibration curve. Repeat until the calibration curve is reproducible.

B. Gas or Water Analysis - Gravimetric option:

Stock solution of VC.

Pipet 40.0 ml of carbon tetrachloride into a tared 50 ml glass stoppered volumetric flask and accurately weigh to 0.1 mg.

Attach a tygon delivery tube to the VC lecture bottle valve. Attach the end of the delivery tube to a piece of glass tubing which has been constricted at one end, flush out the tube with VC, and slowly bubble VC into the  $\text{CCl}_4$  containing volumetric flask until about 5.0 mg of VC has been added. Precautions should be exercised to prevent loss of carbon tetrachloride during this operation. Reweigh the volumetric flask to determine the weight of added VC. Fill the volumetric flask to the 50 ml mark (approximately 100 ppm wt/vol). (These operations should be carried out in a hood).

Transfer 1 ml of the stock solution of VC to a 25 ml volumetric flask and dilute to the 25 ml mark with carbon tetrachloride (approximately 4 ppm w/v).

Transfer 5 ml of the 4 ppm VC solution to a 10 ml volumetric flask and dilute to the 10 ml mark (approximately 2 ppm, w/v). Repeat dilution for a solution approximately 1 ppm, and 0.2 ppm.

Transfer the stock solution to a teflon-lined screw capped bottle. This solution can be kept for extended periods of time. Transfer the diluted solutions to serum vials and cap them with teflon-lined serum cap septa.

Inject 1 ml aliquots of the calibration solutions in the GC equipped with Carbowax 1500 on Carbowax A packed columns and an FID detector. Use Zero nitrogen or helium carrier gas at a flow rate of 60 ml/min. Operate the inlet at 150°C and the column at 60°C. After the VC peak has been eluted, program the column temperature to 150°C to elute solvent. Cool column back to 60°C for follow-on concentrations.

Repeat procedure using a GC equipped with a 4% FFAP on Gas Chrom Q packed column and FID detector. Operate under the same conditions. Prepare a calibration curve to be used be used with water samples.

## Procedure

### Water Sample Analysis

Untreated water samples (1-5 microliter aliquots) are injected directly into the GC.

A 4% FFAP on "Gas Chrom Q" packed column is used. Nitrogen zero gas or helium is used as the carrier gas at a flow rate of 60 ml/min. Inlet temperature is set at 150°C. The column is operated isothermally at 62°C. Detection is by FID.

Report concentration of VC in sample in mg/l.

### Sludge and Scum Samples

Extract 5 grams of sludge or scum sample with 100 ml of tetrahydrofuran (THF). Analyze THF extract in the same manner used for water samples. If VC concentrations are too high, make appropriate dilutions of the THF extracts.

Report concentration of VC in sample in mg /g of sample.

### Air Sample Analysis

Grab samples.

Use a 0.4% Carbowax1500 on Carbopak A packed column. Use nitrogen zero gas or helium as the carrier gas with a flow rate of 60 ml/min. Operate the column and inlet at room temperature. Use a flame ionization detector.

Untreated air samples (1 ml) are injected directly into the GC. VC contamination of syringes requires attention.

Report concentration of VC in gas samples in ppm (v/v).

### Continuous Samples

Use same procedure as previously discussed for calibration of adsorption tube efficiency.

## Quality Control

Duplicate sample analyses are recommended as a quality control check.

## SUMMARY OF REGIONAL ACTIVITIES

This Appendix briefly summarizes the results of the preliminary VC monitoring activities conducted by EPA Regional Offices during the Spring of 1974 at the request of the Task Force. More detailed reports are available from the Regional Offices.

The sampling and analyses were carried out in a very short period of time using new methods, based on the Agency's best scientific judgment. They represent, in the Agency's opinion, the best methods then available. In large measure, the sampling and analysis methods were based on previous analytical studies in which similar chemicals were evaluated. However, they had not been thoroughly tested for accuracy and precision under field conditions.

Prior to and during the sampling and measurement only limited quality control and standardization of procedures could be applied in the time available. The methods utilized were interim procedures which have already been subjected to further modification.

The nature of the PVC manufacturing process results in the escape of VC pulses which could lead to widely fluctuating levels of VC in the ambient air. So, too, changes in air movement may influence concentrations at a given station at any one time. Therefore, the VC data reported are preliminary in nature and are subject to change as additional monitoring is performed. Individual measurements probably underestimate the VC levels due to the possibility of VC leakages and other inaccuracies in the monitoring system.

Region I: Leominster, Massachusetts: Borden Chemical Company (PVC); May 9, 10, 13.

1. One hundred and fifty-seven discrete (grab) ambient air samples were collected on plant property and within a 3.0 mile radius of the plant. The VC concentrations ranged from less than the detectable limit of 0.06 ppm to 6.0 ppm. The samples exceeding 1 ppm were obtained on plant property near the fenceline.
2. Twelve 24-hour integrated ambient air samples were collected at the fenceline on plant property. The VC values ranged from less than the detectable limit of 0.06 ppm to 1 ppm.
3. VC concentrations in three 24-hour composite waste water samples taken from the lagoon effluent ranged from 0.15 to 0.29 ppm.
4. VC concentrations in two sludge samples taken from the lagoon near the outlet measured at the 0.05 - 0.06 ppm level on a wet basis.

5. The plant is located in a residential/industrial area on the edge of Leominster with residential developments adjacent to plant property.

6. Shifting meteorological conditions and rain hampered the sampling program.

Region II: Flemington, New Jersey: Tenneco Chemicals, Inc. (PVC); May 29-31.

1. Forty-three discrete ambient air samples were collected on plant property and within a 2.0 mile radius of the plant. The VC concentrations outside the plant property ranged from less than detectable (0.01 ppm) to 0.05 ppm. On plant property a single sample collected on the dryer building roof contained 5.6 ppm. At ground elevation, the VC concentrations on plant property ranged up to 0.30 ppm.

2. Twenty-three integrated ambient air samples were collected for 24-hour periods on plant property and within 2.0 miles of the plant. The VC values ranged from 0.005 to 0.038 ppm on plant property and from less than detectable to 0.031 ppm outside the plant area.

3. Two integrated one-hour ambient air samples collected within 0.1 mile of the plant showed VC at levels of 0.32 ppm and 0.18 ppm.

4. A maximum level of 20 ppm was detected in three 24-hour composite samples taken from the water effluent discharge into the Bushkill Brook, which immediately flows into the Raritan River. This amounts to approximately 400 lbs/day.

5. VC concentrations in sludge samples taken from the lagoon areas on plant property ranged from less than detectable to 1,000 ppm in wet weight concentrations; however, the concentration at the sludge disposal area was 54 ppm.

6. The plant is located in an area in which manufacturing facilities are interspersed with farmland and relatively large acreage residential properties. There are a number of small communities within a few miles of the plant.

Region III: Delaware City, Delaware: Stauffer Chemical Company (PVC) and Diamond Shamrock Chemical Company (PVC); May 20-22. S. Charleston, West Virginia: Union Carbide Corporation (PVC); May 24.

1. The air sampling and analysis activity was organized around a mobile laboratory equipped with a gas chromatograph using a flame ionization detector. VC levels were later confirmed by mass spectrometer.

2. A single discrete ambient air sample at the fenceline of the Diamond Shamrock plant showed 0.2 ppm VC.

3. Four discrete ambient air samples taken near the Stauffer Chemical plant ranged from 0.3 to 0.7 ppm VC. The highest level was recorded 0.5 miles from the plant and the lower levels at 0.25 miles from the plant.

4. The area immediately adjacent to the Delaware City complex is lightly populated residential areas for several miles.

5. Water samples collected at the Union Carbide plant gave VC values of 1.1 and 0.8 ppm for grab samples at several outfalls and 0.35 for a 24-hour composite. Samples obtained from the Kanawha River did not have a detectable level of VC.

6. Sampling was attempted but was not feasible due to limited time and equipment difficulties at the PVC plants of the Firestone Plastics Company in Perryville, Maryland, and Pottstown, Pennsylvania.

Region IV: Louisville, Kentucky: B.F. Goodrich Chemical Company (PVC); March 19-21 and May 8-16.

1. The initial air monitoring program conducted in March was preliminary to the more extensive program in May which showed significantly higher levels.

2. In May there were 39 discrete ambient air samples collected in the area designated industrial (within 0.8 miles from the plant center). The VC concentrations ranged from less than 0.05 to 5.6 ppm, with 10 samples exceeding 1 ppm. In the area designated residential/ industrial, 149 samples were collected within 0.8 miles of the plant with VC concentrations ranging from less than 0.05 to 33 ppm. The average concentrations at the site registering 33 ppm were between 0.5 and 1 ppm, but 18 samples had concentrations greater than 5.0 ppm. Four samples were obtained in strictly residential areas with VC values of 0.05 to 1.6 being observed. The 1.6 value was 0.8 miles from the plant.

3. Five sampling sites were established within 0.6 miles of the plant for integrated air sampling over 24 hours. VC values ranged from less than 0.001 to 0.53 ppm. The highest value was obtained from a sampling site 0.2 miles from the plant center.

4. Wastewater from the clarifier discharge was measured in March at 2 to 3 mg/l in 24-hour composite samples.

5. Dewatered clarifier sludge and clarifier scum contained 193 and 162 ppm of VC, respectively.

Region V: Painesville, Ohio: Uniroyal, Inc. (PVC) and Robintech, Inc. (PVC); May 9-14.

1. Four of 137 ambient air samples taken at distances up to 3.0 miles from the plant showed levels exceeding 1 ppm of VC with the highest level being 2.26 ppm. Many of the samples were less than 0.1 ppm.

2. Nine 24-hour integrated ambient air samples taken at various distances from the plant showed levels up to 0.2 ppm of VC.

3. VC levels in 11 of 17 water effluent samples were less than 0.2 ppm, with three samples exceeding 1 ppm, including a high of 3.7 ppm.

4. VC levels in nine sludge samples, as the sludge would leave the plant property, ranged from 9 to 3520 ppm.

5. The complex is surrounded by residential areas.

Region VI: Plaquemine, Louisiana: The Goodyear Tire and Rubber Company (PVC) and Dow Chemical Company (VC); April 7-9.

1. There were 31 discrete ambient air samples collected within 3.0 miles of the complex with VC concentrations ranging from less than detectable (.001 ppm) to 7.81 ppm. Most of the readings were less than 1 ppm, with the highest value at the property line.

2. VC concentrations in wastewater effluent measured by 24-hour composites were all below .05 ppm.

3. VC concentrations in residual reactor scrapings at the Goodyear plant ranged from 23 to 31 ppm.

4. The small communities of Morrisonville and Eliza are located less than 1 mile north and northwest respectively of the Goodyear plant. A few homes from Morrisonville extend almost to the north property line of the Goodyear plant.

5. Very limited air sampling was conducted in the Houston area in the vicinity of the plants listed below. However, in view of the inadequacy of this activity, the sampling effort in this area is being continued.

Deer Park, Tex., PVC Plant - Diamond Shamrock Corp., Diamond Shamrock Chemical Co.

Deer Park, Tex., VC Plant - Shell Chemical Co., Industrial Chemicals Division

Houston, Tex., VC Plant - Tenneco, Inc., Tenneco Chemicals, Inc.

Pasadena, Tex., VC Plant - Ethyl Corporation

Region IX: Long Beach, California: B.F. Goodrich Chemical Company (PVC); American Chemical Corporation (VC); American Chemical Corporation (PVC); May 7-10.

1. One hundred and eighty 10-minute integrated ambient air samples were collected within 3.1 miles of the complex. About 11 percent of the

readings exceeded 0.5 ppm, while 5 percent exceeded 1.0 ppm. The maximum value measured was 3.4 ppm in a sample taken 3.1 miles from the plant; however, the average level measured at this point was about 0.5 ppm.

2. Samples of wastewater effluents were composited for 8 to 24 hours and yielded values from 3.5 to 8.9 ppm, with individual samples reading up to 22 ppm.

3. Sludge samples showed values ranging from 290 to 4200 micrograms of VC per gram of dry sludge.

4. The complex is surrounded by residential areas. Within the three mile radius of the plants there are eleven schools.

## PERSISTENCE OF VINYL CHLORIDE

The available information on the stability and persistence of VC in the environment is currently very limited. Some literature and laboratory studies have recently been initiated by industry and by EPA. This discussion summarizes the findings of EPA to-date and particularly the results of research efforts at EPA research facilities undertaken in response to the needs of the Task Force for at least preliminary data on environmental fate. Results of related experiments reported by industry seem to be consistent with the discussion.

### Behavior of Vinyl Chloride in Air

The peak absorption of VC in the ultraviolet region is very far below the solar cutoff of about 2900 Å, indicating that VC would not undergo reaction in sunlight in the absence of other reactive chemicals. When irradiated with simulated solar radiation in the presence of nitrogen oxides (nitric oxide and nitrogen dioxide), VC reacts to form a variety of products. The available laboratory results indicate a rate of reaction of about 8 to 10% per hour for VC, recognizing that reaction rates may vary with concentrations. The direct and indirect reaction products identified included ozone, nitrogen dioxide, carbon monoxide, formaldehyde, formic acid, and formyl chloride. High eye irritation levels were found with human exposure panels which is consistent with the products identified.

The low reaction rate of VC, including reactions in the presence of nitrogen oxides, indicates that within a few miles downwind of VC emission sources VC will persist and can be considered a stable pollutant. The usual meteorological dispersion equations for gases could be applied to approximate concentrations. Because of temperature inversions and the absence of sunlight at night during the fall and winter, buildup of VC might be of particular concern during such periods. Clearly at greater distances from emission sources, VC will have greater opportunity to disperse and degrade.

The noxious gases which are products of VC reactions should not be ignored. In air quality regions with large industrial activities involving large volume production of these chemicals, such products may contribute appreciably on particularly sunny days to eye, nose, throat, and lung irritation.

### Behavior of Vinyl Chloride in Water

The loss of VC from water at constant temperature and pressure depends on the rate of agitation or aeration. Distilled water in a beaker spiked with 16 ppm VC, when rapidly stirred at 22°C with a magnetic stirrer, lost 96% of VC in two hours, while quiescent water at the same concentration lost only 25% VC. There was no significant difference in the rate of VC losses from distilled water, river water, or effluent from a VC plant stirred at the same rate, indicating negligible adsorption effects with particulate matter. Plots of log water concentration versus time give straight lines, indicating volatility to be the only important loss mechanism.

Hydrolysis over a pH range of 4.3 to 9.4 does not appear to be an important pathway for loss of VC from water. Chemical reaction of VC in the clarifier effluent from a VC plant was followed at 50°C for 57 hours at pH 4.3, 8.0, and 9.4 in sealed septum vials. Concentrations indicated that VC at these three pH values decreased at the same rate. This lack of pH dependence suggests that the loss of VC occurred by volatilization rather than hydrolysis, or at least there is a very slow hydrolysis rate. This experiment should be repeated in leak-proof reaction vials.

Very preliminary experiments do not show photolysis as an important pathway for loss of VC in water. However, there are many uncertainties in the experimental techniques, and additional studies are needed in this area.

Earlier theoretical studies are consistent with these experimental results. One study on the transfer of small non-reactive molecules across the air-water interface (as in stream aeration) used a kinetic approach to predict that VC will be rapidly lost from an aqueous solution, with the rate of loss being a function of water turbulence, mixing efficiency, and molecular diameter. Another study, using a thermodynamic approach, predicted a rapid rate of evaporation of low solubility chlorinated hydrocarbons, including compounds of low vapor pressure.

Despite the foregoing efforts there is a general absence of data concerning VC in aquatic systems. It is conceivable that as the result of poor or erratic mixing in lakes or ponds, together with slow but continuous release of VC from sediments and sludges, VC could persist long enough to accumulate biologically, via direct absorption or via the food chain, or to cause other ecological effects.

#### Behavior of Vinyl Chloride in Closed Rooms

Tables 1 and 2 present data concerning concentrations of VC in a typical room following release of a pesticidal spray containing VC.

TABLE 1  
One Hundred and Twenty Second Release of Insect Spray in  
133,000 Liter Room

| SAMPLE | TIME                                     | VC        | COLUMN I | VC       | COLUMN II |
|--------|------------------------------------------|-----------|----------|----------|-----------|
|        |                                          |           | FREON-12 |          | FREON-12  |
| No. 1  | Collected at breathing zone during spray | 41.64 ppm | 8.15 ppm | 41.9 ppm | 7.94 ppm  |
| No. 2  | 15 minutes                               | 16.91     | 3.13     | 17.1     | 3.30      |
| No. 3  | 30 minutes                               | 1.38      | 0.27     | 1.32     | 0.25      |
| No. 4  | 60 minutes                               | 0.08      | 0.018    | 0.061    | 0.018     |
| No. 5  | 120 minutes                              | 0.012     | -        | 0.010    | -         |

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

| SAMPLE | TIME                                   | COLUMN I  |           | COLUMN II |           |
|--------|----------------------------------------|-----------|-----------|-----------|-----------|
|        |                                        | VC        | FREON-12* | VC        | FREON-12* |
| No. 1  | Collected one minute after spray       | 380.1 ppm | 84.8 ppm  | 383.6 ppm | 83.2 ppm  |
| No. 2  | 30 minutes later                       | 52.1      | 9.9       | 48.7      | 10.3      |
| No. 3  | 60 minutes                             | 24.6      | 4.8       | 22.5      | 4.7       |
| No. 4  | 150 minutes                            | 10.3      | 2.1       | 9.3       | 2.2       |
| No. 5  | Collected in adjacent hall 151 minutes | 0.83      | 0.17      | 0.17      | 0.15      |

\*Freon-12 concentrations were determined using hydrocarbon response factors to compare dilution effects; the actual concentration is higher by a factor of 5.3.

#### REFERENCES

1. Unpublished results of experiments and analyses conducted at EPA laboratories in Research Triangle Park, N. C., and Athens, Georgia, during April and May 1974.
2. Unpublished results of experiments on persistence of VC in water conducted by Dow Chemical Company.
3. Tsiroglou, E. C. and J. R. Wallace, "Characterization of Stream Reaeration Capacity," EPA Ecological Research Series Report #EPA-R3-72-012 (October, 1972).
4. MacKay, Donald and Aaron W. Wolkoff, "Rate of Evaporation of Low-Solubility Contaminants from Water Bodies to Atmosphere," Environmental Science & Technology, 7 (7):611-614 (July, 1973).

## HEALTH EFFECTS OF VC

This Appendix presents much of the epidemiological and toxicological data available as of August 1974, on the health effects associated with exposure to VC, together with a few interpretive comments supplementing information presented in the body of the report. However, the Appendix does not present an exhaustive review or evaluation of available information.

Table 1 summarizes the data, collected by CDC/NIOSH, on the confirmed cases of angiosarcoma of the liver in VC/PVC workers in the United States and abroad. A total of 15 occupational cases have been discovered in the United States and confirmed as angiosarcoma of the liver. Of the 15 cases, 2 are still alive and undergoing treatment. Fourteen of the 15 were employed in PVC production plants and the remaining one in a PVC fabrication plant. The average age at death for the U.S. PVC production workers was 48.5 years (with a range from 36 to 61 years) which is about seven years younger than the average age of death from liver cancer in the U.S. male population. Based on the data available for the workers, the latent period for this disease appears to be on the order of twenty years, a period consistent with latencies observed for other occupational, chemically induced cancers.

In the U.S. PVC production worker cases, all of the men were at one time "pot cleaners", required to enter the reactors in order to chip the residue of the chemical reaction from the sides of the "pots." Since the residue often contained pockets of trapped gases that were literally released in the cleaner's face when they were ruptured by his chipping operation, the potential for exposure to high levels of VC while cleaning these tanks was particularly great during the early years of this operation.

Ten cases of worker-related angiosarcoma of the liver have been reported from five foreign countries to date.

Table 2 summarizes the epidemiological data, collected by CDC from the Connecticut Tumor Registry, on five confirmed cases of angiosarcoma of the liver, including one accountant in a PVC fabrication plant and two residents near PVC fabrication plants. The case of occupational exposure occurred in a man who had been employed for 10 years as an accountant in a factory which produces vinyl sheets and processes PVC resins; it is reported that he frequently visited the production area of the plant. Of the two cases who had no occupational exposure to VC or PVC, one was a 73 year-old man who lived his entire life within two miles of a PVC wire insulation plant. The other was an 83 year-old woman, a housewife and retired cook, who had lived for 35 years within one-half mile of the vinyl products plant at which the accountant had been employed.

While these findings establish no causal connection between exposure to PVC and angiosarcoma of the liver, they do raise the possibility of such a relationship. Time will be needed to define the possible risk factors in persons who have worked with PVC since the latency period appears to be so long. Because of the rarity of this tumor, the additional finding in this study of angiosarcoma of the liver in persons who had no occupational exposure to VC, but who may have had community exposure, is also worrisome but again establishes no causal connection. Epidemiologic investigation of additional cases of hepatic angiosarcoma that may be found to have had possible community exposure to VC will be necessary to clarify the significance of these cases.

Tables 3A - 3D present the findings of the MCA-funded mortality study of VC/PVC workers, conducted by Tabershaw/Cooper Associates.

In calculating the risk of death, the usual method is to express the number of deaths which actually occurred as a percentage of the number which would have been expected in a comparable population observed over the same age and time intervals. This statistic is called the Standardized Mortality Ratio (SMR). Using the U. S. male population as the standard population of comparison, the SMRs were calculated for each of the 35 cases of death for which detailed mortality rates are published on a national basis. In the standard population each SMR would be equal to 100. The statistical significance of the deviation of each SMR in the study population from the expected value of 100 was tested. A single asterisk indicates those SMRs which differed significantly from 100 at the 5 percent level, that is, which had a probability of .05 or less of occurring by chance. A double asterisk indicates those which were significant at the 1 percent level. SMRs based on fewer than 5 observed cases were not tested for significance. The overall mortality of the study population is statistically significantly lower than that of the U. S. male population. There were 352 observed deaths compared with 467 expected, for an SMR of 75.

For each job, an exposure score was estimated by industrial hygiene and safety personnel in each plant. A score of 1 was given for low exposure, 2 for medium, and 3 for high. The number of months each worker spent on a given job was multiplied by the appropriate exposure score. The total for each worker was then divided by the total number of months of exposure to give an Exposure Index (EI) for that worker. Table 3A shows the SMRs for workers with an EI below 1.5 versus those at 1.5 or above. The dividing point of 1.5 represents a level halfway between low and medium exposure. Table 3B shows similar results for workers with less than 5 years exposure versus those with 5 years or more.

In order to examine the possible interaction between duration and level of exposure, the study population was divided into 4 groups on the basis of both EI (low vs. high) and duration of exposure (short vs.

long) using the same dichotomization as Tables 3A and 3B. Table 3C shows the results for short versus long exposure in the low EI group, and Table 3A shows the same comparison in the high EI group. When the study population is divided according to length and duration of exposure (Tables 3A and 3B) and combinations of these measurements (Tables 3C and 3D), three major patterns emerge. For malignant neoplasms as a whole, the SMR increases with increasing exposure, whether measured by level, duration, or both. In the high exposure group with 5 years or more exposure (Table 3D) there are 36 observed cases and 26.11 expected. For cardiovascular - renal diseases as a group, there are also increases in the SMR with increasing exposure, but the number of observed cases remain less than expected, the differences being statistically significant in all groups except the high exposure, long duration group. For all other causes, there are no consistent relationships with exposure.

Within the malignant neoplasms, the largest (although not statistically significant) SMR is in cancers of the buccal cavity and pharynx, with 5 observed, 2.84 expected, and an SMR of 189. However, Tables 3A and 3D show that all these cases have an EI below 1.5, and 4 out of 5 have less than 5 years exposure.

Cancer of the digestive system shows no excess in the study population as a whole. However, in those workers with EIs of 1.5 or higher, there are 12 observed cases where 9.14 are expected (Table 3A). In the subgroup of the above workers with 5 years or more exposure, there are 11 observed cases and 7.47 expected.

Respiratory cancer shows a slight excess in the total group, and a similar pattern for different exposure categories, with 13 observed versus 10.28 expected when the EI is 1.5 or higher, and 12 observed versus 8.50 expected when, in addition, the duration of exposure is 5 years or more.

Malignant neoplasms of other and unspecified sites show an excess in the total group, and an increase with both level and duration of exposure (Tables 3A and 3B). The relationship with exposure is more pronounced, since those with exposures of less than 5 years have fewer cases than expected.

The lymphosarcomas, although occurring at about the expected rate when the whole group is considered, are concentrated almost entirely in the high exposure long duration group. In that category there are 4 cases observed and 1.84 expected.

The Tabershaw/Cooper Study is based on an examination of 328 death certificates. The authors acknowledge three areas where bias might have entered: (a) choice of the U.S. male population as the

standard, (b) absence of 15% of the study population (untraceable), and (c) discovery, as the study ended, of a group of 1500 workers whose exposures occurred up to 35 years ago and who are not included in the study group. Since the latency period for angiosarcoma of the liver is averaging 18 years at least, it would appear desirable to examine the data for these 1500 workers.

In addition to the Tabershaw/Cooper study several other epidemiological studies presented during the recent OSHA hearings suggest the possibility of a multiple cancer risk.

Table 4 summarizes many of the published and unpublished toxicological and epidemiological studies of human and animal exposures to VC. A list of the references cited in Table 4 completes this Appendix.

Table 1  
OCCUPATIONAL CASES OF LIVER ANGIOSARCOMA

| Occupation                            | Country        | Case # | BIRTH DATE | 1st VC/PVC Work | Diagnosis of Angiosarcoma | Age at Diagnosis | Yrs. 1st VC/PVC Work To Diagnosis | Total Yrs. VC/PVC Exposure | Date of Death |
|---------------------------------------|----------------|--------|------------|-----------------|---------------------------|------------------|-----------------------------------|----------------------------|---------------|
| 1. VC Monomer Production              | Sweden         | 01     | 00-00-11   | 00-00-45        | 00-00-72                  | 61               | 27                                | 23                         | 00-00-72      |
| 2. PVC Polymerization                 | United States  | 01     | 00-00-22   | 12-09-48        | 03-00-71                  | 49               | 22                                | 16                         | 03-03-73      |
|                                       | United States  | 02     | 00-00-34   | 11-15-55        | 05-00-70                  | 36               | 14                                | 13                         | 09-23-71      |
|                                       | United States  | 03     | 00-00-15   | 11-28-45        | 12-00-73                  | 58               | 28                                | 28                         | 12-19-73      |
|                                       | United States  | 04     | 00-00-24   | 07-06-52        | 0E-00-67                  | 43               | 15                                | 15                         | 01-07-68      |
|                                       | United States  | 05     | 00-00-12   | 06-19-44        | 04-00-64                  | 52               | 20                                | 18                         | 04-09-64      |
|                                       | United States  | 06     | 00-00-29   | 01-17-62        | 02-00-74                  | 45               | 12                                | 12                         | Alive         |
|                                       | United States  | 07     | 05-03-22   | 08-00-44        | 00-00-68                  | 45               | 24                                | 18                         | 03-23-68      |
|                                       | United States  | 08     | 05-06-20   | 10-07-45        | 08-00-61                  | 41               | 15                                | 15                         | 08-29-61      |
|                                       | United States  | 09     | 00-00-31   | 05-28-43        | 03-01-74                  | 43               | 29                                | 17                         | Alive         |
|                                       | United States  | 10     | 08-16-13   | 06-00-51        | 05-00-68                  | 55               | 17                                | 17                         | 05-10-68      |
|                                       | United States  | 11     | 05-27-09   | 10-14-46        | 03-00-70                  | 61               | 23                                | 23                         | 03-16-70      |
|                                       | United States  | 12     | 11-17-18   | 09-13-49        | 05-00-69                  | 50               | 20                                | 15                         | 05-02-69      |
|                                       | United States  | 13     | 12-01-21   | 08-19-44        | 05-00-74                  | 53               | 30                                | 30                         | 07-04-74      |
|                                       | W. Germany     | 01     | 07-26-31   | 10-14-57        | 00-00-71                  | 40               | 14                                | 14                         | 12-14-71      |
|                                       | W. Germany     | 02     | 06-04-30   | 10-01-57        | 00-00-69                  | 39               | 11                                | 11                         | 01-25-69      |
|                                       | Great Britain  | 01     | 00-00-01   | 00-00-45        | 12-00-72                  | 71               | 26                                | 20                         | 12-00-72      |
|                                       | Norway         | 01     | 12-23-15   | 03-00-50        | 12-20-71                  | 56               | 22                                | 21                         | 01-04-72      |
|                                       | Sweden         | 02     | 00-00-27   | 00-00-51        | 00-00-70                  | 43               | 19                                | 18                         | 00-00-70      |
|                                       | Czechoslovakia | 01     |            |                 |                           |                  |                                   |                            |               |
|                                       | Czechoslovakia | 02     |            |                 |                           |                  |                                   |                            |               |
| 3. PVC Compounders, Fabricators, Etc. | United States  | 14     | 11-04-27   | 11-11-51        | 00-00-69                  | 41               | 17                                | 4                          | 03-27-69      |
|                                       | United States  | 15     | 00-00-25   | 00-00-00        | 07-00-72                  | 47               | 00                                | 00                         | 02-15-73      |
|                                       | Great Britain  | 02     | 00-00-14   | 00-00-46        | 02-00-70                  | 55               | 24                                | 11                         | 12-00-70      |
| 4. Other VC Exposure                  | W. Germany     | 03     |            |                 |                           | 43               | 14                                |                            |               |

Note: '00' indicates unknown date

SOURCE: NIOSH

Table 2

## CASES OF HEPATIC ANGIOSARCOMA, CONNECTICUT, 1935-1973

| Case No. | Age | Sex | NCI Diagnosis                              | Date of Original Diagnosis | Date of Death | Medical History                                                                                                                                                                                                                                                     | Occupation                                                                                                        | Place of Residence                                              |
|----------|-----|-----|--------------------------------------------|----------------------------|---------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------|
| 1        | 73  | M   | Hepatic Angiosarcoma                       | 11-25-67                   | 12-3-67       | 2 months history of diarrhea, anorexia, and 20 lb weight loss. Intermittent abdominal pain. Non-tender, firm epigastric mass. Died after 9 days with spontaneous ruptured liver leading to shock. Past history of alcohol intake.                                   | Fireman 1917-42<br>Aluminum worker 1942-44<br>Corset cutter 1945-61<br>Retired 1961-67                            | Bridgeport - entire life                                        |
| 2        | 47  | M   | Alcoholic Cirrhosis<br><br>Portal Fibrosis | 1-15-73                    | 2-15-73       | Initial symptoms RUQ abdominal pain with vomiting. Cecal volvulus found, Rx cecopexy, over next 6 weeks pain continued with weakness. RUQ tenderness with 2 FB liver. Diagnosed by needle biopsy on 1-15-73. Deteriorated slowly until death 31 days later.         | Accountant - Vinyl Co., 1963-73<br>Accountant - Plastic Belt Co., 1956-63<br>Previously accountant - other states | Bridgeport - 1956-73<br>Previously many locations               |
| 3        | 83  | F   | Hepatic Angiosarcoma                       | 12-19-73                   | 1-22-74       | Admitted 12-2-73 with short history of RUQ abdominal pain radiating to R shoulder. Had RUQ tenderness. Open liver biopsy 12-19-73 showed large tumor. No resection. Deteriorated until death 34 days later.                                                         | Housewife<br>Restaurant cook 35 yrs                                                                               | Stratford 35 years                                              |
| 4        | 76  | F   | Hepatic Angiosarcoma                       | 3-12-50                    | 3-19-50       | 1 month history of anorexia with abdominal pain and back pain. Firm epigastric mass. Died 6 days after admission with carcinomatosis and pulmonary emboli.                                                                                                          | Housewife                                                                                                         | Windsor Locks                                                   |
| 5        | 50  | M   | Hepatic Angiosarcoma                       | -                          | 5-4-73        | Admitted for abdominal pain and jaundice 3-27-73. 4 FB liver. Discharged. Readmitted 4-29-73 with abd distension, general edema, icterus, fever, shaking chills. Rapid downhill course with death due to renal and hepatic failure. Past history of alcohol intake. | Fisherman and carpenter before 1959 Planter 1959-60. Unemployed 1960-73.                                          | Puerto Rico 1923-59<br>New York City 1959-73<br>Bridgeport 1973 |

Table 3A

OBSERVED DEATHS/EXPECTED DEATHS AND STANDARDIZED MORTALITY RATIOS IN VINYL CHLORIDE WORKERS,  
BY ESTIMATED LEVEL OF EXPOSURE

| Cause of death with I.C.D.#number                                   | EI <1.5    |                  | EI ≥1.5    |                  |
|---------------------------------------------------------------------|------------|------------------|------------|------------------|
|                                                                     | obs/exp    | SMR <sup>1</sup> | obs/exp    | SMR <sup>1</sup> |
| All causes                                                          | 188/270.33 | 70**             | 157/195.68 | 80**             |
| Tuberculosis (001-019)                                              | 0/3.38     | 0                | 0/2.33     | 0                |
| Tuberculosis of respiratory system (001-008)                        | 0/3.16     | 0                | 0/2.18     | 0                |
| Malignant neoplasms (140-203)                                       | 37/44.28   | 90               | 41/32.67   | 134              |
| Malignant neoplasms, buccal cavity and pharynx (140-148)            | 5/1.62     | 330              | 0/1.21     | 0                |
| Malignant neoplasms, digestive organs and peritoneum (150-159)      | 7/12.50    | 60*              | 12/9.14    | 141              |
| Malignant neoplasms, respiratory system (160-164)                   | 11/13.56   | 86               | 13/10.28   | 135              |
| Malignant neoplasms, genital organs (170-179)                       | 2/2.30     | 93               | 1/1.43     | 75               |
| Malignant neoplasms, urinary organs (180-181)                       | 1/2.07     | 51               | 0/1.52     | 0                |
| Malignant neoplasms, other and unspecified sites (190-199)          | 9/6.57     | 146              | 8/4.52     | 190              |
| Leukemia and leukemia (204)                                         | 1/2.18     | 49               | 2/1.57     | 136              |
| Lymphomas, lymphatic and hematopoietic tissues (200-203, 205)       | 1/3.48     | 31               | 5/2.54     | 212              |
| Diabetes mellitus (240)                                             | 5/3.65     | 146              | 2/2.65     | 81               |
| Major cardiovascular and renal diseases (330-334, 400-438, 592-594) | 84/120.11  | 75**             | 69/66.99   | 85*              |
| Ventricular diseases affecting QRS (330-334)                        | 7/14.42    | 52**             | 6/10.05    | 64               |
| Myocardial infarction and rheumatic heart dis. (400-402, 410-415)   | 3/3.98     | 80               | 2/2.85     | 75               |
| Arteriosclerotic heart disease (420)                                | 68/76.94   | 92               | 51/58.05   | 95               |
| Myocardial infarction (421, 422)                                    | 0/4.20     | 0                | 1/2.89     | 38               |
| Myocardial heart disease (440-443)                                  | 1/5.48     | 19               | 2/3.86     | 56               |
| Other myocardial diseases (444-447)                                 | 1/1.52     | 70               | 2/1.07     | 201              |
| Coronary atherosclerosis and renal sclerosis (592-594)              | 0/2.50     | 0                | 0/1.77     | 0                |
| Influenza and pneumonia (480-493)                                   | 5/5.80     | 92               | 0/4.13     | 0                |
| Liver of stomach and esophagus (540, 541)                           | 1/2.21     | 48               | 1/1.60     | 68               |
| Appendicitis (580-583)                                              | 0/0.39     | 0                | 0/0.27     | 0                |
| Gastritis, duodenitis, enteritis and colitis (543, 571, 572)        | 0/0.68     | 0                | 1/0.63     | 171              |
| Cirrhosis of liver (581)                                            | 0/0.76     | 0                | 1/0.55     | 196              |
| Hypertrophic of prostate (610)                                      | 2/8.90     | 23               | 1/6.64     | 16               |
| Syphilis, gonorrhea and ill-defined conditions (780-795)            | 0/0.25     | 0                | 0/0.14     | 0                |
| All other diseases (residual)                                       | 0/4.22     | 0                | 1/3.09     | 34               |
| Motor vehicle accidents (810-835)                                   | 14/21.90   | 68*              | 6/15.89    | 41**             |
| Other accidents (800-802, 840-862)                                  | 8/19.00    | 45**             | 9/13.46    | 72               |
| Suicide (961, 970-979)                                              | 11/17.83   | 66*              | 6/12.67    | 50**             |
| Homicide (984, 980-985)                                             | 9/9.73     | 98               | 7/7.02     | 107              |
| Number of workers                                                   | 4632       |                  | 3052       |                  |
| Person-years                                                        | 45354      |                  | 32108      |                  |

<sup>1</sup>SMR's adjusted for deaths with cause unknown.

\*Significant at 5% level.

\*\*Significant at 1% level.

†International Classification of Diseases

SOURCE: Tabershaw Cooper Associates, Inc., Epidemiological Study of Vinyl Chloride Workers, Final Report

Table 3B

OBSERVED DEATHS/EXPECTED DEATHS AND STANDARDIZED MORTALITY RATIOS IN VINYL CHLORIDE WORKERS  
BY DURATION OF EXPOSED EMPLOYMENT

| Cause of death with I.C.D. number                                   | <60 months |                  | ≥60 months |                  |
|---------------------------------------------------------------------|------------|------------------|------------|------------------|
|                                                                     | obs/exp    | SMR <sup>1</sup> | obs/exp    | SMR <sup>1</sup> |
| All causes                                                          | 94/140.53  | 67**             | 251/329.30 | 76**             |
| Tuberculosis (001-019)                                              | 0/2.23     | 0                | 0/3.55     | 0                |
| Tuberculosis of respiratory system (001-003)                        | 0/2.07     | 0                | 0/3.33     | 0                |
| Malignant neoplasms (140-205)                                       | 13/19.96   | 78               | 65/57.61   | 116              |
| Malignant neoplasms, buccal cavity and pharynx (140-148)            | 4/0.70     | 688              | 1/2.16     | 47               |
| Malignant neoplasms, digestive organs and peritoneum (150-159)      | 2/5.26     | 46               | 17/16.56   | 106              |
| Malignant neoplasms, respiratory system (160-184)                   | 3/5.32     | 65               | 21/18.51   | 116              |
| Malignant neoplasms, genital organs (170-179)                       | 0/0.99     | 0                | 3/2.76     | 112              |
| Malignant neoplasms, urinary organs (180-181)                       | 0/0.83     | 0                | 1/2.79     | 37               |
| Malignant neoplasms, other and unspecified sites (190-199)          | 2/3.40     | 71               | 15/8.23    | 187              |
| Leukemia and leukemia (204)                                         | 1/1.25     | 96               | 2/2.53     | 81               |
| Lymphocytoma, lymphatic and hematopoietic tissues (200-203, 205)    | 1/2.01     | 60               | 5/4.07     | 126              |
| Diabetes mellitus (260)                                             | 2/1.80     | 134              | 5/4.54     | 113              |
| Major cardiovascular and renal diseases (330-334, 400-468, 592-594) | 28/51.45   | 65**             | 125/157.39 | 81**             |
| Vascular lesions affecting CNS (330-334)                            | 4/5.97     | 81               | 9/18.71    | 45**             |
| Rheumatic fever & chronic rheumatic heart dis. (400-403, 410-416)   | 2/2.39     | 101              | 3/4.53     | 68               |
| Arteriosclerotic heart disease (420)                                | 21/32.54   | 78*              | 98/105.39  | 96               |
| Rheumatic endocarditis (421, 422)                                   | 0/1.79     | 0                | 1/5.35     | 20               |
| Hypertensive heart disease (440-443)                                | 1/2.42     | 49               | 2/7.01     | 30               |
| Other hypertensive disease (444-447)                                | 0/0.79     | 0                | 3/1.82     | 170              |
| Chronic & unspecified nephritis & renal sclerosis (592-594)         | 0/1.55     | 0                | 0/2.76     | 0                |
| Influenza and pneumonia (480-493)                                   | 3/2.93     | 123              | 2/7.09     | 49               |
| Ulcer of stomach and duodenum (540, 541)                            | 1/1.07     | 112              | 1/2.78     | 37               |
| Appendicitis (550-553)                                              | 0/0.24     | 0                | 0/0.43     | 0                |
| Hernia and intestinal obstruction (560, 561, 570)                   | 0/0.42     | 0                | 1/1.10     | 93               |
| Gastritis, duodenitis, enteritis and colitis (543, 571, 572)        | 1/0.40     | 301              | 0/0.92     | 0                |
| Cirrhosis of liver (581)                                            | 1/4.49     | 26               | 2/11.18    | 18               |
| Hypertrophy of prostate (610)                                       | 0/0.07     | 0                | 0/0.33     | 0                |
| Symptoms, senility and ill-defined conditions (780-795)             | 1/2.28     | 53               | 0/5.09     | 0                |
| All other diseases (residual)                                       | 4/11.97    | 40               | 16/26.34   | 63*              |
| Motor vehicle accidents (810-835)                                   | 10/16.14   | 75               | 7/16.65    | 43**             |
| Other accidents (800-802, 840-952)                                  | 7/12.94    | 65*              | 10/17.82   | 58*              |
| Suicide (963, 970-979)                                              | 6/6.34     | 114              | 10/10.28   | 100              |
| Heatstroke (964, 980-985)                                           | 1/5.80     | 20               | 0/6.20     | 0                |
| Number of workers                                                   | 2955       |                  | 4134       |                  |
| Person-years                                                        | 34201      |                  | 43240      |                  |

<sup>1</sup>SMR's adjusted for deaths with cause unknown.

\*Significant at 5% level.

\*\*Significant at 1% level.

Table 3C

OBSERVED DEATHS/EXPECTED DEATHS AND STANDARDIZED MORTALITY RATIOS IN VINYL CHLORIDE WORKERS  
WITH EXPOSURE INDICES BEICW 1.5, BY DURATION OF EXPOSED EMPLOYMENT

| Cause of death with I.C.D. number                                   | ≤60 months exposure |                  | ≥60 months exposure |                  |
|---------------------------------------------------------------------|---------------------|------------------|---------------------|------------------|
|                                                                     | obs/exp             | SMR <sup>1</sup> | obs/exp             | SMR <sup>1</sup> |
| All causes                                                          | 56/89.23            | 63**             | 132/181.28          | 73**             |
| Tuberculosis (001-019)                                              | 0/1.41              | 0                | 0/1.97              | 0                |
| Tuberculosis of respiratory system (001-008)                        | 0/1.31              | 0                | 0/1.85              | 0                |
| Malignant neoplasms (140-205)                                       | 8/12.86             | 73               | 29/31.46            | 95               |
| Malignant neoplasms, buccal cavity and pharynx (140-145)            | 4/0.45              | 1036             | 1/1.17              | 88               |
| Malignant neoplasms, digestive organs and peritoneum (150-159)      | 1/3.43              | 34               | 6/9.08              | 68               |
| Malignant neoplasms, respiratory system (160-164)                   | 2/3.58              | 65               | 9/10.00             | 93               |
| Malignant neoplasms, genital organs (170-179)                       | 0/0.68              | 0                | 2/1.62              | 127              |
| Malignant neoplasms, urinary organs (180-181)                       | 0/0.55              | 0                | 1/1.53              | 67               |
| Malignant neoplasms, other and unspecified sites (190-199)          | 1/0.97              | 120              | 8/4.43              | 187              |
| Leukemia and aleukemia (204)                                        | 0/0.79              | 0                | 1/1.40              | 73               |
| Lymphosarcoma, lymphatic and hematopoietic tissues (200-203,205)    | 0/1.26              | 0                | 1/2.23              | 46               |
| Diabetes mellitus (260)                                             | 2/1.15              | 203              | 3/2.50              | 124              |
| Major cardiovascular and renal diseases (330-334, 400-468, 592-594) | 21/33.38            | 73**             | 63/86.82            | 75**             |
| Vascular lesions affecting CVS (330-334)                            | 2/3.93              | 59               | 5/10.51             | 49*              |
| Rheumatic fever & chronic rheumatic heart dis. (400-402, 410-416)   | 2/1.50              | 155              | 1/2.49              | 41               |
| Arteriosclerotic heart disease (420)                                | 16/21.14            | 88               | 52/57.87            | 93               |
| Nonrheumatic endocarditis (421, 422)                                | 0/1.18              | 0                | 0/3.02              | 0                |
| Hypertensive heart disease (440-443)                                | 1/1.58              | 74               | 0/3.90              | 0                |
| Other hypertensive disease (444-447)                                | 0/0.50              | 0                | 1/1.02              | 101              |
| Chronic & unspecified nephritis & renal sclerosis (592-594)         | 0/0.97              | 0                | 0/1.53              | 0                |
| Influenza and pneumonia (480-493)                                   | 3/1.86              | 188              | 2/3.95              | 53               |
| Ulcer of stomach and duodenum (540, 541)                            | 0/0.68              | 0                | 1/1.53              | 67               |
| Appendicitis (550-553)                                              | 0/0.15              | 0                | 0/0.24              | 0                |
| Hernia and intestinal obstruction (560, 561, 570)                   | 0/0.27              | 0                | 0/0.61              | 0                |
| Gastritis, duodenitis, enteritis and colitis (543, 571, 572)        | 0/0.26              | 0                | 0/0.51              | 0                |
| Cirrhosis of liver (581)                                            | 1/2.80              | 42               | 1/6.09              | 16               |
| Hyperplasia of prostate (610)                                       | 0/0.05              | 0                | 0/0.20              | 0                |
| Symptoms, senility and ill-defined conditions (780-795)             | 0/1.43              | 0                | 0/2.79              | 0                |
| All other diseases (residual)                                       | 4/7.45              | 63               | 10/12.92            | 79               |
| Motor vehicle accidents (810-835)                                   | 3/9.87              | 35               | 5/9.22              | 56               |
| Other accidents (800-802, 840-862)                                  | 3/7.98              | 44               | 8/9.85              | 83               |
| Suicide (963, 970-979)                                              | 1/4.08              | 86               | 6/5.66              | 109              |
| Homicide (964, 980-985)                                             | 0/3.55              | 0                | 0/3.43              | 0                |
| Number of workers                                                   | 1715                |                  | 2317                |                  |
| Person-years                                                        | 21418               |                  | 23920               |                  |

<sup>1</sup>SMR's adjusted for deaths with cause unknown.

\*Significant at 5% level.

\*\*Significant at 1% level.

Table 3D

OBSERVED DEATHS/EXPECTED DEATHS AND STANDARDIZED MORTALITY RATIOS IN VINYL CHLORIDE WORKERS  
WITH EXPOSURE INDICES OF 1.5 OR GREATER, BY DURATION OF EXPOSED EMPLOYMENT

| Cause of death with I.C.D. number                                   | <60 months exposure |                  | ≥60 months exposure |                  |
|---------------------------------------------------------------------|---------------------|------------------|---------------------|------------------|
|                                                                     | obs/exp             | SMR <sup>1</sup> | obs/exp             | SMR <sup>1</sup> |
| All causes                                                          | 38/47.93            | 79               | 119/147.81          | 81 <sup>2</sup>  |
| Tuberculosis (001-019)                                              | 0/0.76              | 0                | 0/1.57              | 0                |
| Tuberculosis of respiratory system (001-002)                        | 0/0.71              | 0                | 0/1.48              | 0                |
| Malignant neoplasms (140-205)                                       | 5/6.57              | 96               | 36/26.11            | 141              |
| Malignant neoplasms, buccal cavity and pharynx (140-148)            | 0/0.23              | 0                | 0/0.99              | 0                |
| Malignant neoplasms, digestive organs and peritoneum (150-159)      | 1/1.67              | 76               | 11/7.47             | 150              |
| Malignant neoplasms, respiratory system (160-164)                   | 1/1.79              | 71               | 12/8.50             | 144              |
| Malignant neoplasms, genital organs (170-179)                       | 0/0.29              | 0                | 1/1.41              | 73               |
| Malignant neoplasms, urinary organs (180-181)                       | 0/0.26              | 0                | 0/1.26              | 0                |
| Malignant neoplasms, other and unspecified sites (190-199)          | 1/1.10              | 107              | 7/3.51              | 204              |
| Leukemia and aplukemia (204)                                        | 1/0.44              | 288              | 1/1.13              | 90               |
| Lymphosarcoma, lymphatic and hematopoietic tissues (200-203, 205)   | 1/0.71              | 178              | 4/1.84              | 222              |
| Diabetes mellitus (260)                                             | 0/0.61              | 0                | 2/2.04              | 100              |
| Major cardiovascular and renal diseases (330-334, 400-468, 592-594) | 7/16.54             | 54 <sup>2*</sup> | 62/70.46            | 90               |
| Vascular lesions affecting CNS (330-334)                            | 2/1.87              | 135              | 4/8.19              | 50               |
| Rheumatic fever & chronic rheumatic heart dis. (400-402, 410-416)   | 0/0.82              | 0                | 2/2.04              | 100              |
| Arteriosclerotic heart disease (420)                                | 5/10.41             | 61 <sup>*</sup>  | 46/47.65            | 98               |
| Nonrheumatic endocarditis (421, 422)                                | 0/0.57              | 0                | 1/2.32              | 44               |
| Hypertensive heart disease (440-443)                                | 0/0.75              | 0                | 2/3.10              | 66               |
| Other hypertensive disease (444-447)                                | 0/0.27              | 0                | 2/0.81              | 253              |
| Chronic & unspecified nephritis & renal sclerosis (592-594)         | 0/0.54              | 0                | 0/1.23              | 0                |
| Influenza and pneumonia (480-493)                                   | 0/0.99              | 0                | 0/3.13              | 0                |
| Ulcer of stomach and duodenum (540, 541)                            | 1/0.35              | 362              | 0/1.25              | 0                |
| Appendicitis (550-553)                                              | 0/0.08              | 0                | 0/0.19              | 0                |
| Hernia and intestinal obstruction (560, 561, 570)                   | 0/0.14              | 0                | 1/0.49              | 209              |
| Gastritis, duodenitis, enteritis and colitis (543, 571, 572)        | 1/0.14              | 904              | 0/0.41              | 0                |
| Cirrhosis of liver (581)                                            | 0/1.56              | 0                | 1/5.08              | 20               |
| Hyperplasia of prostate (610)                                       | 0/0.01              | 0                | 0/0.13              | 0                |
| Symptoms, senility and ill-defined conditions (780-795)             | 1/0.80              | 156              | 0/2.30              | 0                |
| All other diseases (residual)                                       | 0/4.02              | 0                | 6/11.86             | 51 <sup>*</sup>  |
| Motor vehicle accidents (810-835)                                   | 7/6.05              | 146              | 2/7.43              | 28               |
| Other accidents (800-802, 840-962)                                  | 4/4.73              | 107              | 2/7.96              | 26               |
| Selficide (963, 970-979)                                            | 3/2.40              | 158              | 4/4.62              | 88               |
| Homicide (984, 980-985)                                             | 1/2.18              | 58               | 0/2.76              | 0                |
| Number of workers                                                   | 1240                |                  | 1817                |                  |
| Person-years                                                        | 12828               |                  | 19305               |                  |

<sup>1</sup>SMR's adjusted for deaths with cause unknown.<sup>2</sup>Significant at 5% level.<sup>3</sup>Significant at 1% level.

Table 4  
SUMMARY OF TOXICOLOGICAL AND EPIDEMIOLOGICAL STUDIES ON VINYL CHLORIDE

| Authors                                                                                    | Species | Sex    | No.    | EXPOSURE                                                                     |      | HUMAN DATA                                        |                                               | Observations                                                                                                                                                                                                                                                                                                                                                                                                           | Pathology     |
|--------------------------------------------------------------------------------------------|---------|--------|--------|------------------------------------------------------------------------------|------|---------------------------------------------------|-----------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------|
|                                                                                            |         |        |        | Mrs.<br>per<br>Day                                                           | Days | Conc.<br>ppm                                      | Total Dose<br>ppm-Days                        |                                                                                                                                                                                                                                                                                                                                                                                                                        |               |
| Von Ottingen<br>(1955)                                                                     | Human   |        |        |                                                                              |      | 12,000<br>10,000<br>25,000                        |                                               | Dangerous<br>Narcosis<br>Produced symptoms of dizziness, disorientation,<br>headache and burning sensation on soles of feet.                                                                                                                                                                                                                                                                                           |               |
| Gabor<br>Mecca-Radu<br>Manta<br>(1962)<br>Chem. Abstract                                   | Human   |        | 82     | Workers exposed to DDT,<br>Benzene, Hexachlorocyclo-<br>hexane, VC, PVC.     |      |                                                   |                                               | Blood: Decrease in catalase<br>Increase in peroxidase, indophenoloxidase<br>and glutathione<br>Changes occurred during second year of work.                                                                                                                                                                                                                                                                            | None reported |
| Lester<br>Greenberg<br>Adams<br>(1963)                                                     | Human   | M<br>F | 3<br>3 | Twice per day<br>for 3 days,<br>5 min. sessions<br>at 6 hours in-<br>tervals |      | 0<br>4,000<br>8,000<br>12,000<br>16,000<br>20,000 | 0<br>83.3<br>166.7<br>250.0<br>333.2<br>416.7 | 1/5 slightly dizzy<br>0/6 had any effects<br>1/6 slightly dizzy<br>2/6 definitely dizzy<br>5/6 dizzy, nausea, blurred vision and heaving<br>symptoms stopped after exposure<br>6/6 intoxicated, one with persistent headaches<br>50% level of no effect is 1.3%<br>No statement about repeated exposures                                                                                                               | None reported |
| Gabor<br>Radu<br>Preda<br>Abudean<br>Jumef<br>Anca<br>Valenzky<br>(1964)<br>Chem. Abstract | Human   |        | 78     | PVC Workers                                                                  |      |                                                   |                                               | Decrease plasma albumin<br>Increased S and S globulin<br>Decrease in B/R for serum lipoproteins<br>Decrease in serum cholinesterase<br>Decrease in pseudo cholinesterase<br>Normal blood catalase<br>Normal serum pyruvic acid                                                                                                                                                                                         | None reported |
| Grigorescu<br>Toba<br>(1966)<br>Chem. Abstract                                             | Human   |        |        | Experimental: PVC Workers<br>Control: Other clinically<br>healthy people     |      |                                                   |                                               | Hypothesis: $\text{VC} + \text{H}_2\text{O} \rightarrow \text{chloral} + \text{chloroacetic acid}$ (1).<br>Results: (1) was found in 80% of exptl. people, but<br>in none of controls.<br>Most of + findings were in people exposed 2-5 years.<br>In these cases, $\alpha$ -globulin is higher, $\beta$ -globulin is<br>lower than people with no (1) in urine. Capacity<br>to metabolize (1) decreased after 2 years. | None reported |

## HUMAN DATA

| Authors                              | Species | Sex    | No.      | EXPOSURE     |      |    |      | Conc. ppm | Total Dose ppm-Days | Observations                                                                                                                                                                                                                                 | Pathology                                                                                                                                                                                                                                                   |
|--------------------------------------|---------|--------|----------|--------------|------|----|------|-----------|---------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                      |         |        |          | Hrs. per Day | Days |    |      |           |                     |                                                                                                                                                                                                                                              |                                                                                                                                                                                                                                                             |
| Harris Adams (1967)                  | Human   |        | 2        | -            | -    | -  | -    | -         | -                   |                                                                                                                                                                                                                                              | One worker had knee cap and toes involved in the acro-osteolysis. Other worker only hands.                                                                                                                                                                  |
| Wilson McCormick Tatum Creech (1967) | Human   | M      | 31       | -            | -    | -  | -    | -         | -                   | No cases of acro-osteolysis diagnosed in 1000 individuals who handled finished resin or used for plastic product production<br><br>Age range of affected workers 26-47. Incubation period greater than 12 months of polycleaning experience. | 31/3000 (3%) workmen associated with polymerization found to have acro-osteolysis.<br><br>22/31 Acro-osteolysis associated with Reynaud's symptoms.                                                                                                         |
| Earceta Stewart Murchler (1969)      | Human   | M      | 13       | 7.5          | 1    | 50 | 15.6 | 250       | 78.1                | Breath decay curves, 0 to 20 hrs. after exposure were measured. Level in breath at 4 hrs. is $\approx$ 1%. No adverse effects noted. About the same set of breath decay curves following occupational exposure.                              | None Reported                                                                                                                                                                                                                                               |
| Kudryautseva (1970) Abstract         | Human   | M<br>F | 50<br>43 | -            | -    | -  | -    | -         | -                   | 1. Changes in ECG: rhythm, conductance, polarization.<br>2. Increase in systolic index.                                                                                                                                                      | None Reported.                                                                                                                                                                                                                                              |
| Viola (1970) Unpublished             | Human   | -      | 1        | 8            | 1095 |    |      |           |                     | Acro-osteolysis symptoms, Reynaud's syndrome, aversion to fats, enlarged liver<br>Raynaud's syndrome                                                                                                                                         | Aerometry:<br>(VC) on factory filters at air discharge time: 2,000 ppm<br>(VC) at point of worker entry: 2,000 ppm in plants where acro-osteolysis occurred-150 ppm (max) in plant with no blast<br>(VC) on gateway and other parts of plant: 10 to 15 ppm. |
|                                      |         |        | 5        | 8            | 1825 |    |      |           |                     | Enlarged liver, minor liver insufficiency.                                                                                                                                                                                                   |                                                                                                                                                                                                                                                             |
|                                      |         |        | 15       |              |      |    |      |           |                     |                                                                                                                                                                                                                                              |                                                                                                                                                                                                                                                             |
|                                      |         |        | 500*     |              |      |    |      |           |                     | 13/500 had acro-osteolysis. Olfactory threshold is 0.1 to 1%. Acute nervous symptoms become evident when it is easily perceptible.                                                                                                           |                                                                                                                                                                                                                                                             |
|                                      |         |        |          |              |      |    |      |           |                     | *In several other factories                                                                                                                                                                                                                  |                                                                                                                                                                                                                                                             |

## HUMAN DATA

| Authors                                                          | Species | Sex | No.  | Hrs.<br>per<br>Day         | Conc. Dose<br>Days ppm | Total<br>ppm-Days | Observations                                                                                                                                                                                                                                                                                                                                                                                                                                           | Pathology                                                                                                                                                                                                                                                      |
|------------------------------------------------------------------|---------|-----|------|----------------------------|------------------------|-------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Dismann<br>Cook<br>Waterhouse<br>Magnuson<br>Ditchcock<br>(1971) | Human   |     | 5011 | 21,510                     | Haz-years Experience   |                   | Conditions associated with hand cleaning of polymerizers.<br>There appeared to be correlation between reactor degassing time and acro-osteolysis.                                                                                                                                                                                                                                                                                                      | 25 cases of acro-ostenolysis.<br>16 other individuals questionable.<br>Acro-osteolysis appears to be systemic rather than local disease.<br>Reynaud's phenomenon was statistically related to acro-osteolysis.                                                 |
| Dodson<br>Dinson<br>Whitchouse<br>Naser<br>Magnuson<br>(1971)    | Human   | M   | 4    | 1-23 Months                |                        |                   | All patients had worked as PVC reactor-vessel cleaners.<br>Neg. Ca and P balance in one subject.<br>Plethysmographic abnormalities were present in 3 subjects.<br>Esophageal motility within normal limits.<br>Catecholamine, -Hydroxyindole Acetic Acid excretion normal.<br>All other numerous clinical laboratory investigations negative.                                                                                                          | Reynaud's phenomenon anteceded osteolytic lesions in all four subjects.<br>18F scintiscans correlated with radiographic lesions.<br>No liver enlargement or hypothyroidism.<br>Additional smaller abnormalities found in ulnar styloid, os calcis and patella. |
| Kramer<br>Mutchler<br>(1971)                                     | Human   | M   | 98   | -Up to 25 years Experience |                        |                   | Performed statistical correlation between several clinical measurements and total dose and time-weighted average VC concentration.<br><br>2 liver function indices show a positive correlation with total dose (abnormally high).<br>a) Icterus index<br>b) Bromsulphalein<br>3 other indices are dose-related but are not outside normal limits: a) systolic and diastolic blood pressure.<br>b) hemoglobin negative correlation.<br>c) beta-protein. | None reported.                                                                                                                                                                                                                                                 |

# HUMAN DATA

| Authors                                                            | Species | Sex | No. | Hrs/Day | Days | EXPOSURE |            | OBSERVATIONS                                        | PATHOLOGY                                                                                                                                                                                                                                                                                                                                                                      |
|--------------------------------------------------------------------|---------|-----|-----|---------|------|----------|------------|-----------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                                                    |         |     |     |         |      | Conc.    | Total Dose |                                                     |                                                                                                                                                                                                                                                                                                                                                                                |
|                                                                    |         |     |     |         |      | ppm.     | ppm-days   |                                                     |                                                                                                                                                                                                                                                                                                                                                                                |
| Neyerson<br>Neier<br>(1972)<br>Abstract                            | Human   | -   | 1   | .       |      |          |            |                                                     | Acroosteolysis<br><br>Had unique papular skin lesions which have been described only in PVC workers                                                                                                                                                                                                                                                                            |
| Narkowicz<br>McDonald<br>Fathiere<br>Kerzner<br>(1972)<br>Abstract | Human   | -   | -   |         |      |          |            |                                                     | Describes acroosteolysis symptoms. Incidence is <3% among workers                                                                                                                                                                                                                                                                                                              |
| 47<br>Lange<br>Johne<br>Stein<br>Veltman<br>(1973)                 | Human   | -   | 11  |         |      |          |            | Ages 29-52 Reactor cleaners<br>2-15 yrs. employment | Latent period: 14-34 years in 11 patients; 7 and 11 years in other 2 patients.<br>Acro-osteolysis symptoms.<br>Peripheral vessel stenosis.<br>Thrombopeny (low count) is the first objective symptom described in all patients; lung fibrosis originating in portal system, largespleen, impaired lung function; 10% mortality. This is the first objective symptom described. |

# HEPATIC DATA

## EXPOSURE

| Authors | Species | Sex | No. | Hrs. per day | Days | Conc. ppm | Total Dose ppm-days | Observations | Pathology |
|---------|---------|-----|-----|--------------|------|-----------|---------------------|--------------|-----------|
|         |         |     |     |              |      |           |                     |              |           |

20 PVC workers were studied out of 45 with suspected skin problems, 30 to 56 years old.

## Pathology

Liver enlarged in 13/20.  
Pain in Rt. upper abdomen in 2/20.  
Hyperlipidemia has been diagnosed in 1967 after 6 years in 1/20.  
Jaundice history in 1955 before exposure in 1968. Liver dysfunction was diagnosed, no alcoholism. Spleenomegaly in 7/20.  
Total bilirubin was 1 mg/100 (which is upper normal limit) in 3/20. Bromsulphthalein test was abnormal in 19/20 (75% retention after 45 minutes).  
SGOT was >12 mU/ml in 17/20. SGPT was elevated (15-30) in 14/20.  
Alkaline phosphatase was >48 u/ml in 2/20 Hypothrombocytopenia (<150x 10<sup>3</sup>/mm<sup>3</sup>) was found 19/20 (<100x10<sup>3</sup>/mm<sup>3</sup>).  
Acro-osteolysis was seen in 4/20.  
Arteriole veins of esophagus in 3/20.  
Liver histology: Collagen transformation of walls of sinusoids in 5/20. Focal activation of Kupfer cells in 16/20. Focal fatty infiltration in 14/20. Fibrosis of septa and capsule in 14/20. Intralobular and portal spaces in 2/20.  
Additional pathology parameters were not included in immunological tests were done.

Table 4  
SUMMARY OF TOXICOLOGICAL AND EPIDEMIOLOGICAL STUDIES ON VINYL CHLORIDE

ANIMAL DATA

| Authors                                    | ANIMALS |     |     |            |                   | EXPOSURE           |                        | Observations                                                                                                       | Pathology |
|--------------------------------------------|---------|-----|-----|------------|-------------------|--------------------|------------------------|--------------------------------------------------------------------------------------------------------------------|-----------|
|                                            | Species | Sex | No. | Hrs/day    | Days              | Conc.<br>ppm       | Total Dose<br>ppm-days |                                                                                                                    |           |
| Von Ottingen<br>(1955)<br>(Review Article) | Cats    | ND  | ND  | ND         | ND                | ND                 | ND                     | VC is promptly excreted by lungs; 82% is eliminated after inhalation stops                                         |           |
|                                            | Cats    | ND  | ND  | <4         | 1                 | 100,000 to 130,000 | <1,200                 | Blood VC concentration reaches 15-17 mg%                                                                           |           |
|                                            | Cats    | ND  | ND  | <4         | 1                 | 180,000            | <30,000                | This concentration causes same intra-auricular pressure reduction as 13,000 ppm dichloroethylene, 30,000 ppm ether |           |
|                                            | Cats    | ND  | ND  | <4         | 1                 | 200,000            | <33,000                | Cardiac insufficiency                                                                                              |           |
|                                            | Cats    | ND  | ND  | 4          | 1                 | 250,000 to 300,000 | <40,000 to 50,000      | Even this does not produce complete cardiac failure                                                                |           |
|                                            | Cats    | ND  | ND  | ND         | ND                | ND                 | ND                     | Blood levels are 40 mg% at time of cardiac arrest, 27-30 mg% at time of respiratory arrest                         |           |
|                                            | Rabbits | ND  | ND  | 1 min.     | 1                 | 170,000            | 118                    | This is the narcotic concentration                                                                                 |           |
|                                            | Dogs    |     |     |            |                   |                    |                        |                                                                                                                    |           |
|                                            | Mice    | ND  | ND  | 1 min.     | 1                 | 86,000 to 123,000  | 60 to 85               | This is the narcotic concentration                                                                                 |           |
|                                            | Dogs    | ND  | ND  | <4         | 1                 | 160,000            | <12,000                | Cardiac irregularities, ECG abnormalities                                                                          |           |
|                                            | Dogs    | ND  | ND  | 3          | 7 for several wks | 10,000             | 475                    | No major change in liver or kidney                                                                                 |           |
|                                            | Dogs    | ND  | ND  | 3          | 7 for several wks | 200,000            | 9,500                  | Marked salivation, vomiting, respiratory arrest                                                                    |           |
|                                            | Mice    | ND  | ND  | 10 min.    | 1                 | 245,000 to 295,000 | 1,700 to 2,040         | This is the lethal range for 10 minutes exposure                                                                   |           |
|                                            | G. Pigs | ND  | ND  | short time | 1                 | 200,000 to 400,000 | ND                     | All killed                                                                                                         |           |

# ANIMAL DATA

| Authors                                                                                              | ANIMALS                                                  |     |     |         |         | EXPOSURE     |                        | Observations                                                                                                                                                                                                                                                      | Pathology                                                                           |
|------------------------------------------------------------------------------------------------------|----------------------------------------------------------|-----|-----|---------|---------|--------------|------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
|                                                                                                      | Species                                                  | Sex | No. | Hrs/day | Days    | Conc.<br>ppm | Total Dose<br>ppm-days |                                                                                                                                                                                                                                                                   |                                                                                     |
| Von Oettingen<br>(1955)<br>Revision Article<br>Continued                                             | G. Pigs                                                  | ND  | ND  | 0.5-1   | 1       | 100,000      | 2,000 to<br>4,000      | Dangerous to life.                                                                                                                                                                                                                                                |                                                                                     |
|                                                                                                      | G. Pigs                                                  | ND  | ND  | 0.5-1   | 1       | 5,000        | 100 to<br>200          | Higher concentrations than this cause severe lung edema and hyperemia of liver and kidney                                                                                                                                                                         |                                                                                     |
|                                                                                                      | G. Pigs                                                  | ND  | ND  | 0.5-1   |         | ND           |                        | Order of toxicity is: carbon tetrachloride > chloroform > VC > ethyl chloride                                                                                                                                                                                     |                                                                                     |
| Mastromatteo<br>Fisher<br>Christie<br>Danziger<br>(1959)<br>Fisher<br>Christie<br>Danziger<br>(1960) | Mice                                                     | ND  | 5   | 0.5     | 1       | 100,000      | 2,080                  | Sequential effects were: 1. irritation, 2. increased motor activity, 3. twitching, 4. tremor, incoordination, 5. unconscious, 6. deep narcosis. All animals recovered in 5 minutes.                                                                               | Mice: Light lung engorgement, kidney swelling; Rats and G. Pigs: same lung picture. |
|                                                                                                      | Rats                                                     | ND  | 5   | 0.5     | 1       |              |                        |                                                                                                                                                                                                                                                                   |                                                                                     |
|                                                                                                      | G. Pigs                                                  | ND  | 5   | 0.5     | 1       |              |                        |                                                                                                                                                                                                                                                                   |                                                                                     |
|                                                                                                      | Number of animals and duration of exposure same as above |     |     |         |         | 200,000      | 4,160                  | 1/5 mice died after 30 minutes, same symptoms as above but appeared sooner. Guinea pigs unsteady for 20 min. after exposure.                                                                                                                                      | Lung engorgement, no edema in all species. One rat had fatty liver.                 |
|                                                                                                      | Number of animals and duration of exposure same as above |     |     |         |         | 300,000      | 6,250                  | 5/5 mice and 5/5 rats died; 1/5 guinea pigs died; 4/5 guinea pigs recovered in 25 minutes.                                                                                                                                                                        | Liver and kidney was congested, tracheal epithelium damaged                         |
|                                                                                                      | Number of animals and duration of exposure same as above |     |     |         |         | 400,000      | 8,330                  | 2/5 guinea pigs died                                                                                                                                                                                                                                              | Some symptoms, more severe                                                          |
| Torkelson (!)<br>Cyan<br>Rosen<br>(1961)                                                             | Rats                                                     | M   | 10  | 7       | (5d/wk) | 500          | 14,000                 | Growth and gross appearance were normal. Liver/body weight ratio and absolute liver weight larger than control in males. Liver/body weight and absolute liver weight not larger than control in females. Blood SGOT, SGPT, SUN, alkaline phosphatase were normal. | Central lobular liver degeneration. Kidney tubular damage.                          |
|                                                                                                      |                                                          | F   | 10  | 7       | (4.5Mo) |              |                        |                                                                                                                                                                                                                                                                   |                                                                                     |

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