

NATIONAL INVENTORY OF SOURCES AND
EMISSIONS OF VINYL CHLORIDE (1973)

Chemical Process Sources Division
and
Pollution Data Analysis Division
Air Pollution Control Directorate

APCD 75-1
February 1975

ABSTRACT

Only recently has recognition been given to vinyl chloride hazards. In 1973, there were two vinyl chloride monomer producers and four polyvinyl chloride resin manufacturers in Canada. Because emissions data are scarce, an emission factor approach using values developed by the Environmental Protection Agency of the United States has been used to estimate the vinyl chloride emissions from these plants.

Vinyl chloride atmospheric emissions in Canada have been estimated to be 6568 tons for the base year 1973. Table 1 gives a breakdown of emissions by type of manufacturing process and by company. Of the total emissions, about 89% was released by polyvinyl chloride resin manufacturing plants and about 10% by vinyl chloride monomer manufacturers. In addition, the plastics industry, which processes polyvinyl chloride into end-use plastic products, released about 1% of total vinyl chloride emissions.

RÉSUMÉ

Ce n'est que tout dernièrement que l'on a reconnu le danger du chlorure de vinyle. En 1973, le Canada comptait deux producteurs de chlorure de vinyle et quatre fabricants de chlorure de polyvinyle. Afin de déterminer les quantités d'émissions de chlorure de vinyle et comme les données pertinentes étaient peu nombreuses, on a adopté une méthode basée sur les facteurs d'émission, en utilisant les valeurs mises au point par l'Environmental Protection Agency des États-Unis.

Les émissions de chlorure de vinyle dans l'atmosphère ont donc été évaluées à 6568 tonnes pour l'année 1973, au Canada. Le tableau 1 en donne une répartition par procédé de fabrication et par compagnie. Environ 89% des émissions sont attribuables à la fabrication du chlorure de polyvinyle et près de 10% à la production de chlorure de vinyle. De son côté, l'industrie des plastiques qui transforme le chlorure de polyvinyle est responsable d'environ 1% des émissions.

TABLE 1 SUMMARY OF VINYL CHLORIDE EMISSIONS IN CANADA - 1973

Emission Source	Estimated emissions	
	Tons	Percent
VINYL CHLORIDE MANUFACTURING		
Dow Chemical of Canada Ltd. Sarnia, Ontario	350	5.3
Gulf Oil Canada Ltd. Varennnes, Quebec	300	4.6
	650	9.9
POLYVINYL CHLORIDE MANUFACTURING		
Esso Chemical Canada Sarnia, Ontario	2250	34.2
B.F. Goodrich Canada Ltd. Niagara Falls, Ontario	1350	20.6
B.F. Goodrich Canada Ltd. Shawinigan, Quebec	1350	20.6
Monsanto Chemical Co. LaSalle, Quebec	900	13.7
	5 850	89.1
PROCESSING OF POLYVINYL CHLORIDE		
Various Plants	68	1.0
	68	1.0
TOTAL	6 568	100.0

TABLE OF CONTENTS

	PAGE
ABSTRACT	i
RESUME	ii
LIST OF TABLES	v
LIST OF FIGURES	vi
1 INTRODUCTION	1
1.1 Background	1
1.2 Toxicity of Vinyl Chloride	2
2 EMISSIONS OF VINYL CHLORIDE FROM VINYL CHLORIDE MONOMER (VCM) MANUFACTURING	3
2.1 Detailed Process Description	3
2.2 Sources of Emissions	5
2.3 Production and Emission Factor Data	5
3 EMISSIONS OF VINYL CHLORIDE FROM POLYVINYL CHLORIDE (PVC) RESIN MANUFACTURING	6
3.1 Detailed Process Description	6
3.2 Sources of Emissions	7
3.3 Production and Emission Factor Data	9
4 EMISSIONS OF VINYL CHLORIDE FROM PROCESSING OF PVC RESIN	10
5 EMISSIONS OF VINYL CHLORIDE FROM OTHER SOURCES	11
REFERENCES	12

LIST OF TABLES

TABLE		PAGE
1	SUMMARY OF VINYL CHLORIDE EMISSIONS IN CANADA - 1973	ii
2	VCM PLANT POINT SOURCE LOCATIONS	5
3	VCM PLANTS AND LOCATIONS - 1973	5
4	EMISSIONS FROM VCM PLANTS	6
5	PVC PLANT POINT SOURCE LOCATIONS	7
6	PVC PLANTS AND LOCATIONS - 1973	9
7	EMISSIONS FROM PVC PLANTS	10

LIST OF FIGURES

FIGURE		PAGE
1	VCM PROCESS FLOW DIAGRAM	4
2	PVC PROCESS FLOW DIAGRAM	8

1 INTRODUCTION

1.1 Background

The purpose of this report is to identify and quantify the sources of emissions to the atmosphere of vinyl chloride for the year 1973. Vinyl chloride monomer (VCM) is a hydrocarbon derivative with the chemical formula $\text{CH}_2 = \text{CHCl}$. At normal temperatures and pressures, it is a colourless, flammable gas with a boiling point of 7°F (-14°C) and an odor similar to that of ether (1).

Vinyl chloride gas is stable in air. In the bulk liquid state, however, it tends to polymerize, or form long chains of linked vinyl chloride molecules. The resulting polymer is a resin known as polyvinyl chloride (PVC). As vinyl chloride monomer is generally stored as a liquid under pressure in commercial applications, a stabilizer such as phenol is added to prevent premature polymerization (2).

All of the vinyl chloride in Canada is used to make polyvinyl chloride resin*(3). Plasticizers and other additives are then combined with the resin to produce a variety of PVC plastics. These are among the most important plastics available today, and are used in the manufacture of such familiar products as garbage bags, food wrappers, detergent bottles, piping, flooring, and records.

Two companies in Canada manufacture vinyl chloride: Dow Chemical Ltd. at Sarnia, Ontario, and Gulf Oil Canada Ltd. at Varennes, Quebec. Both operations crack ethylene dichloride (EDC) to produce vinyl chloride. Emissions from vinyl chloride manufacturing account for about 10% of total vinyl chloride emissions.

* Since June, 1974, vinyl chloride has been banned from use as a spray can propellant. It is believed that none was ever used for this purpose in Canada.

Four plants in Canada receive the vinyl chloride monomer from the two primary manufacturers, for the purpose of producing polyvinyl chloride resin. These are Esso Chemical Canada at Sarnia, Ontario; B.F. Goodrich Chemicals Ltd. at Niagara Falls, Ontario and Shawinigan, Quebec; and Monsanto Chemical Co. at LaSalle, Quebec (3). Basically, the process consists of mixing monomer with water and a catalyst in a reactor, recycling unreacted monomer, and drying and storing the resulting polymer (3). Emissions of vinyl chloride from polyvinyl chloride manufacturing constitute approximately 89% of the total emissions.

The finished polyvinyl chloride contains small amounts of residual monomer, typically 50-1000 ppm, but sometimes as much as 1% (4,5). Some or all of this monomer may be released by the many plastics fabricators using polyvinyl chloride as a raw material (3). Emissions of vinyl chloride from this source are estimated to be 1% of the total emissions.

1.2 Toxicity of Vinyl Chloride

It has been known for many years that workers in polyvinyl chloride plants develop an abnormally high incidence of acro-osteolysis, which produces distortion of the skin and bones of the hands and feet. However, it was not until early 1974 that it was announced that several workers in a PVC plant in the United States had died from angiosarcoma. Angiosarcoma is a rare and fatal liver cancer. The average length of time that the American workers, diagnosed as suffering from this cancer, had been exposed to vinyl chloride was 19 years (7). Since the discovery of the link between vinyl chloride and cancer, there have been increased efforts on the part of researchers and regulatory bodies to determine acceptable levels of vinyl chloride in the air. Although there have been several more angiosarcoma deaths in the United States and Europe, to date none have been reported in Canada.

2 EMISSIONS OF VINYL CHLORIDE FROM VINYL CHLORIDE MONOMER
(VCM) MANUFACTURING

2.1 Detailed Process Description

There are three commonly used methods of producing vinyl chloride monomer (8). These are:

- oxychlorination of ethylene
- pyrolysis of ethylene dichloride
- vapour phase reaction of acetylene and hydrogen chloride.

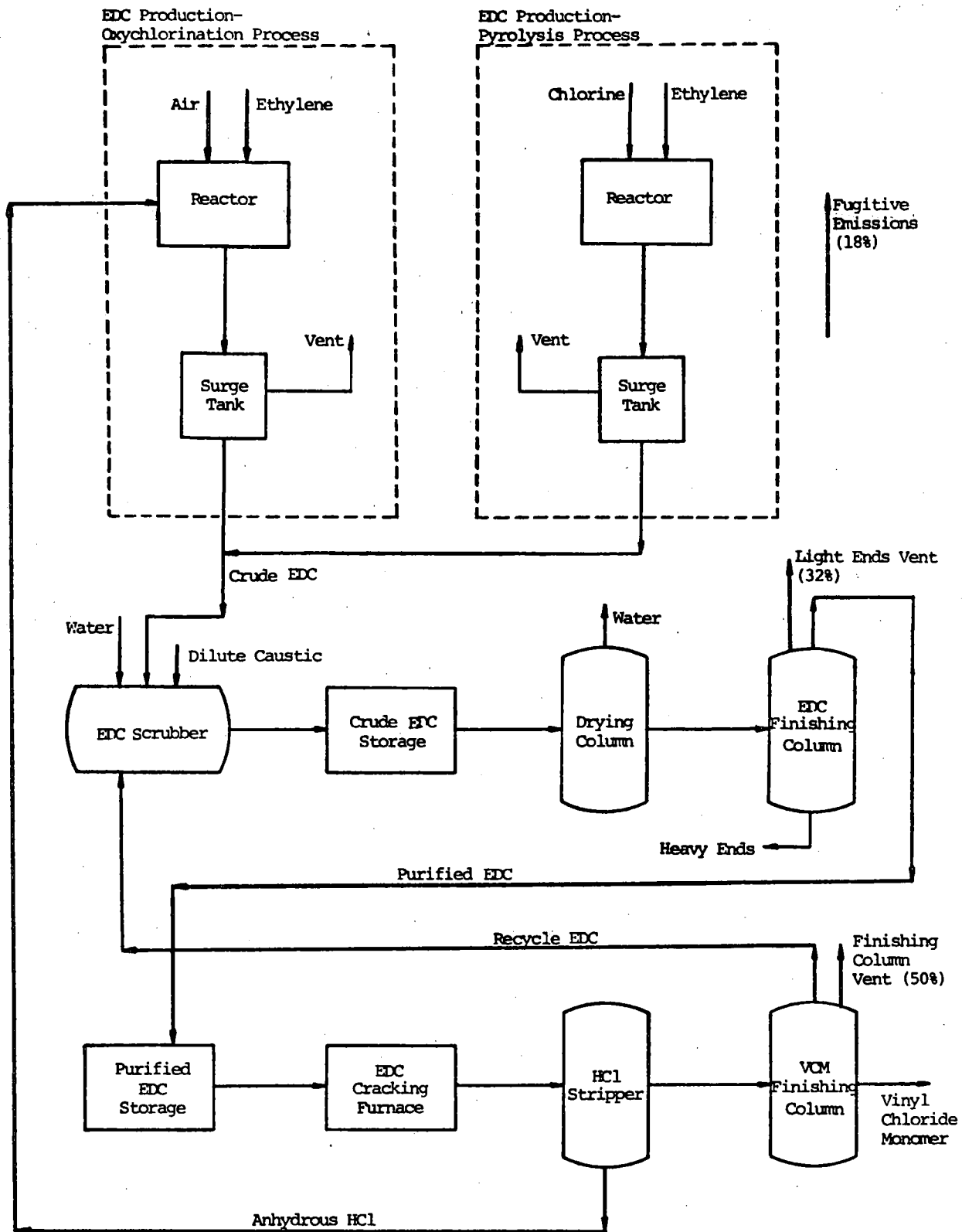
All three processes are continuous, conducted in an enclosed system, and are relatively easy to control. The oxychlorination process is used by Gulf Oil at Varennes while the pyrolysis method is employed at Sarnia by Dow (8).

Both the oxychlorination and pyrolysis processes involve production of the intermediate product ethylene dichloride (EDC), which is then cracked to form vinyl chloride (3). The two processes differ, however, in their methods of producing the EDC. In the oxychlorination process, oxygen in air is reacted with ethylene and hydrogen chloride to form EDC. In the pyrolysis process, EDC is obtained by reacting ethylene with chlorine.

After the EDC has been produced by one of the two above-mentioned reactions it is processed through a scrubber, then to a drying column, and finally, to a finishing column. The purified EDC is stored, then sent to an EDC cracking furnace. Hydrogen chloride is removed in an HCl stripper, and the vinyl chloride is routed to a VCM finishing column. The VCM is stored and the residue from the finishing column may be sent to an EDC recovery tower where uncracked EDC is recovered and recycled (3,9).

The vapour phase reaction, which is not used in Canada, involves combining acetylene and hydrogen chloride directly to produce VCM without passing through the intermediate EDC stage.

A flow diagram for the VCM processes used in Canada is shown in Figure 1.



* Percentage values in parentheses are estimated contributions to total plant emissions.

FIGURE 1 VCM PROCESS FLOW DIAGRAM (3, 9) *
(COMBINED OXYCHLORINATION AND PYROLYSIS PROCESSES)

2.2 Sources of Emissions

The locations in a VCM plant from which emissions are likely to emanate are shown in Table 2.

TABLE 2 VCM PLANT POINT SOURCE LOCATIONS (3)

Point source of VCM emissions	% of total plant emissions (Estimated)
EDC finishing column light ends vent	32
VCM finishing column vent	50
Fugitive (leaks from valves, flanges, seals, pumps and storage facilities)	18

2.3 Production and Emission Factor Data

The two VCM manufacturers in Canada and their estimated production capacities are shown in Table 3.

TABLE 3 VCM PLANTS AND LOCATIONS - 1973 (10)

VCM Plant and location	VCM Capacity (million lb/yr)
Dow Chemical of Canada Ltd. Sarnia, Ontario	140
Gulf Oil Canada Ltd. Varenes, Quebec	120
TOTAL	<u>260</u>

Both plants are currently being operated at capacity in an effort to meet the demand from PVC producers (3).

An emission factor of 0.5 lb VCM/100 lb VCM produced has been used to reflect the level of emissions from these plants (3). This emission factor is based upon data presented in a study by the Monsanto Research Corporation for the United States Environmental Protection Agency (11). The resulting emission quantities are summarized in Table 4.

TABLE 4 EMISSIONS FROM VCM PLANTS - 1973

VCM Plant and location	Estimated VCM emissions (short tons)
Dow Chemical of Canada Ltd. Sarnia, Ontario	350
Gulf Oil Canada Ltd. Varennnes, Quebec	300
TOTAL	<u>650</u>

3 EMISSIONS OF VINYL CHLORIDE FROM POLYVINYL CHLORIDE (PVC) RESIN MANUFACTURING

3.1 Detailed Process Description

Polyvinyl chloride resin manufacturing is a batch process in which vinyl chloride monomer is allowed to polymerize, or link up to form long chains of molecules. There are three common polymerization processes in use (8):

- suspension polymerization
- emulsion polymerization
- mass polymerization

More than 95% of the PVC resin in Canada is produced by the suspension process (3) and, therefore, it is the only process discussed herein. The suspension process is one in which polymerization is carried out in an aqueous medium at a temperature of 100-160 °F and a pressure of 80-180 psig (2) in the presence of an organic peroxide catalyst and an emulsifier (6). The reaction requires 10 to 20 hours (6), during which time about 85% of the VCM is converted to PVC (1). The reactor contents are discharged to a stripper, where unreacted VCM is removed and directed to a condenser for recycling. The wet PVC is transferred to a slurry tank, and then to a centrifuge and dryer where the water is removed. A cyclone controls emissions from the dryer vent. Dried PVC is removed to silo storage (1, 2, 3). A flow diagram for the process is shown in Figure 2.

3.2 Sources of Emissions

The locations in a PVC plant from which emissions are likely to emanate are shown in Table 5.

TABLE 5 PVC PLANT POINT SOURCE LOCATIONS (3)

Point source of VMC emissions	% of Total plant emission (Estimated)
Reactor entry/purge	8.4
Reactor vent	1.7
VCM condenser vent	13.5
Slurry tank vent	11.7
Dryer stack	23.6
Bulk storage	3.4
Fugitive (leaks from valves, flanges, seals, pumps, and VCM feed transfer facilities)	37.7



一、
 二、
 三、
 四、
 五、
 六、
 七、
 八、
 九、
 十、
 十一、
 十二、
 十三、
 十四、
 十五、
 十六、
 十七、
 十八、
 十九、
 二十、

一、
 二、
 三、
 四、
 五、
 六、
 七、
 八、
 九、
 十、
 十一、
 十二、
 十三、
 十四、
 十五、
 十六、
 十七、
 十八、
 十九、
 二十、

3.3 Production and Emission Factor Data

The four PVC plants being operated in Canada and their estimated production capacities are shown in Table 6.

TABLE 6 PVC PLANTS AND LOCATIONS - 1973 (10)

PVC Plant and location	PVC Capacity (million lb/yr)
Esso Chemical Canada Sarnia, Ontario	100
B.F. Goodrich Canada Ltd. Niagara Falls, Ontario	60
B.F. Goodrich Canada Ltd. Shawinigan, Quebec	60
Monsanto Chemical Co. LaSalle, Quebec	40
TOTAL	260

The manufacture of PVC resin constitutes the largest source of VCM emissions to the atmosphere. Studies conducted in the United States have shown that between three and eight percent of the VCM feed is emitted (13). The losses from PVC manufacturing will vary with the age of the plant, operating practices, and the level of abatement technology being used (3).

Because of the heavy demand for PVC products all plants were assumed to be operating at capacity (12). An emission factor of 4.5 lb VCM/100 lb PVC produced was taken to be representative of the plants in Canada (11).

The resulting emission quantities are summarized in Table 7.

TABLE 7 EMISSIONS FROM PVC PLANTS - 1973

PVC Plant and location	Estimated VCM emissions (short tons)
Esso Chemical Canada Sarnia, Ontario	2250
B.F. Goodrich Canada Ltd. Niagara Falls, Ontario	1350
B.F. Goodrich Canada Ltd. Shawinigan, Quebec	1350
Monsanto Chemical Co. LaSalle, Quebec	900
TOTAL	5850

4 EMISSIONS OF VINYL CHLORIDE FROM PROCESSING OF PVC RESIN

Finished PVC resin is used to manufacture many end-use plastic products. All grades of PVC contain residual monomer. The concentration of the residual monomer is a function of resin production techniques and operating practices. The concentration range of this residual monomer is typically 50 to 1000 ppm (14). Because most PVC fabrication processes employ thermal fluxing, a portion of the residual VCM is released during this operation.

Statistics released by the Society of the Plastics Industry of Canada indicate a total PVC resin consumption of 271.5 million pounds for 1973 (15). This is made up of Canadian PVC production plus imports from Japan and the United States.

The current level of VCM emissions from PVC fabrication plants is estimated to be about 68 tons per year. This estimate is based on the assumptions that all of the resin used in Canada in 1973 (271.5 million pounds) contained an average of 500 ppm residual VCM and that virtually all of this residual monomer is released to the atmosphere during the fabrication process (3).

5 EMISSIONS OF VINYL CHLORIDE FROM OTHER SOURCES

Release of all residual monomer contained in PVC was accounted for in the preceding section. Although factual data are lacking, it is likely that there are trace amounts of monomer remaining in end-use polyvinyl chloride. This monomer may eventually be released by diffusion, although this is a very slow process at ambient temperatures. At somewhat elevated temperatures, however, such as at an open dump, monomer release may take place at a faster rate.

Some of the end-use products made of PVC eventually are discarded and require disposal. It has been estimated that 0.25% of refuse is PVC and that this will rise to 1% by 1980 (16). Some of the waste PVC is incinerated. The products of combustion of PVC include water, carbon dioxide, carbon monoxide, phosgene, hydrogen chloride, aromatic hydrocarbons, and sometimes trace amounts of vinyl chloride (17, 18, 19).

Although emissions of vinyl chloride from miscellaneous sources are assumed to exist, they cannot presently be quantified and are assumed to be negligible.

REFERENCES

1. Lafleur, R.J., Vinyl Chloride, Surveillance Division, Air Pollution Control Directorate, Environment Canada, Ottawa, Ontario (June 21, 1974).
2. TRW Systems Group, Air Pollutant Emission Factors, National Technical Information Service, Washington, D.C., Publication PB-206 924, p. 4-51 (April 1970).
3. Gibson, A.B., Personal Memorandum. Abatement and Compliance Branch, Air Pollution Control Directorate, Environment Canada, Ottawa, Ontario (October 18, 1974).
4. Thomas, R.S., Vinyl Chloride - Potential Air Pollution Problems, Chemistry Division, Air Pollution Control Directorate, Environment Canada, Ottawa, Ontario (July 17, 1974).
5. Monkman, J.L., Personal Memorandum. Chemistry Division, Air Pollution Control Directorate, Environment Canada, Ottawa, Ontario (July 26, 1974).
6. Smith, W. Mayo, Ed., Manufacture of Plastics, Volume One, Reinhold Publishing Corp., New York, N.Y. (1964).
7. Anon, "Battle Lines Drawn on Vinyl Chloride Issue", Chemical and Engineering News, p. 16 (February 25, 1974).
8. Gibson, A.B., Personal Memorandum. Abatement and Compliance Branch, Air Pollution Control Directorate, Environment Canada, Ottawa, Ontario (June 25, 1974).
9. Shreve, R.N., Chemical Process Industries, McGraw-Hill, New York, N.Y., p. 681 (1957).
10. Anon, "Product Profile: Vinyl Chloride", Canadian Chemical Processing, p. 42 (January 1974).
11. Hedley, W.H. et al, Potential Pollutants from Petrochemical Processes, Final Report by the Monsanto Research Corporation, Dayton, Ohio, for the United States Environmental Protection Agency, pp. 198-202 (December 1973).
12. Barnes, A., "Plastic Resin Shortage Continues", The Globe and Mail, Toronto, Ontario (October 1, 1974).
13. Schweitzer, G.E., Environmental Concerns Beyond the Work-Place, Presentation to the Working Group on Toxicity of Vinyl Chloride and Polyvinyl Chloride, New York Academy of Sciences, New York (May 11, 1974).

14. Vinyl Chloride Task Force, Preliminary Assessment of Environmental Problems Associated with Vinyl Chloride and Polyvinyl Chloride - Report on the Activities and Findings of the Vinyl Chloride Task Force for the United States Environmental Protection Agency (September, 1974).
15. Plastics Industry Council (Society of the Plastics Industry of Canada), Canadian Plastic Resin Consumption 1973, Don Mills, Ontario, p. 11 (May 1974).
16. "Blame on Plastics - Reasonable", Technica, Vol. 22 No. 6 (1973).
17. Boettner, E.F. and Weiss, R., "An Analytical System for Identifying the Volatile Pyrolysis Products of Plastics", American Industrial Hygiene Association Journal, Vol. 28 No. 6, p. 540 (November - December 1967).
18. Woolley, W.D., "Decomposition Products of PVC for Studies of Fires", British Polymer Journal, Vol. 3 No. 4, p. 190 (July 1971).
19. Schuler, M. and Borla, L., "PVC and Air Hygiene", Chemical Rundschau, Vol. 25 No. 2 (January 12, 1972).

LIBRARY
CANADA CENTRE FOR INLAND WATERS
867 LAKESHORE ROAD
BURLINGTON, ONTARIO, CANADA
L7R 4A6