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SCREENING STUDY TO DEVELOPMENT BACKGROUND INFORMATION AND DETERMINE THE SIGNIFICANCE OF AIR CONTAMINANT EMISSIONS FROM PESTICIDE PLANTS

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ABSTRACT

In this study, available background information is developed and the significance of air contaminant emissions from the manufacture of six pesticides determined. Pesticides studied are (1) insecticides: methyl parathion and toxaphene; (2) herbicides: MSMA and trifluralin; (3) Fungicide and wood preservation: pentachlorophenol; and (4) fumigant: paradichlorobenzene.

Background information is gathered from published data and responses to the questionnaires sent to the pesticide manufacturing firms. Based on the available data, production projections are made up to the year 1980. A list of manufacturers of each pesticide is presented. Manufacturing processes, raw and waste material handling, air contaminant emission sources, quantity or quality, and pollutants, together with their present practical control methods are discussed.

Significance of air contaminant emissions from the pesticide industries is evaluated on the basis of available data on the emission quantities and/or toxicity of the pollutant(s) emitted. Gaps in the data required to make a complete evaluation of significance are identified and recommendations to fill those gaps are made.

SUMMARY

The essential findings of this study can be summarized as follows:

Pesticide Production Inventory

(1) A severe lack of availability of p st and present production data on individual pesticides exists. The U.S. Tariff Commission is the main source of published data on production; however, its lists often are incomplete. Some of the lists are not presented by individual pesticides, but instead by groups of pesticides, such as aldrin-toxaphene or methanearsonic acid salts.

(2) Available published data and expert opinion from the industry and other knowledgeable people outside the industry were carefully evaluated to develop a production table for each pesticide from 1970 to 1980. No estimate on the number of new plants to be built and/or plants to be significantly modified is made.

(3) A list of manufacturers of each pesticide in the United States is included, including the plant (company) name and location. Estimates of the design capacity of existing plants and their production are provided.

Manufacturing Processes

(1) One manufacturing process for each pesticide is identified.

(2) The manufacturing process is briefly described in terms of the steps involved in the production process, aided by simple reaction chemistry and simple production flow sheets.

Raw and Waste Material Handling

(1) Essential raw materials are enumerated. All hazardous materials are identified.

(2) Precontionary safety measures taken by manufacturers to safeguard the health of employees are described. (3) Simple flowsheets for waste handling during the manufacture of each pesticide are provided, identifying the waste disposal technique used.

Air Contaminant Emissions, Sources, and Rates

(!) A table of or contaminant emissions and their sources from manufacturing processes and waste disposal systems is developed.

(2) Where possible, air contaminant emission rates are calculated on the basis of simple reaction chemistry or where available are provided by manufacturing plants.

Air Contaminant Control

(1) Air contaminants arising from production processes are controllable by most of the methods used in the general chemical industries to prevent dusts, fumes, and gases from leaving the production plant and/or its waste treatment site.

(2) The present level of the air contaminant control for each posticide industry is evaluated, where enough information is available from the manufacturers.

(3) Nationwide air contaminant emissions and the present emission control situation are estimated.

Control Costs

(1) Cost estimates are presented only for those companies which submitted such information in response to the survey. While a few companies provided some data on the cost of control in their plants, the operating conditions necessary for an adequate evaluation of the same are not provided. This part of the research, together with the economic impact on the industry due to the imposition of the best available control technique, is not pursued because of resource limits for this study.

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Significance of Emissions from Pesticide Plants

Determination of the significance of the air contaminant emission in each posticide industry is made by identifying the candidate pollutant(s), their quality or emission (where possible), and toxicity.

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SCREENING STUDY TO DEVELOP BACKGROUND INFORMATION AND DETERMINE THE SIGNIFICANCE OF AIE CONTAMINANT EMISSIONS FROM PESTICIDE PLANTS

SECTION I

CONCLUSIONS

The prinicipal conclusions to be drawn from the information derived in the study are as follows:

(1) Most companies are unwilling, for proprietary reasons, to provide their production data to contractors. Published data are incomplete and do not provide a basis upon which to develop a definite trend for forecasting future production. However, forecasts have been provided based on projected raw material availability and demand in agricultural production and other and uses.

(2) Essential health and safety precautionary measures adopted by nost firms are transport of materials in closed systems and requirement for the use of protective clothing such as coveralls, rubber gloves, safety glasses or goggles, hard hats, face shields, and respirators.

(3) Sources of air contaminant emissions vary from one pesticide plant to another. The usual sources are reactor vents, vents along the transport lines, raw material unloading area, product packaging area, and waste and by-product recovery and disposal systems.

(4) Simple process chemistry is not sufficient in determining the quality and quantity of the air contaminant emissions tecause variations in the production process. (5) The identified emissions consist of particulates, gases, and vapors. Each pesticide plant emits into the atmosphere at least one pollutant which may require control. Some are known to create odor nuisance and visibility problems. In some cases, odor nuisance may be experienced, but the odorous compounds are not known. Very little information is available on the emission rates because few companies conduct in-house sampling programs. The popular and most pratically applicable technique used in controlling emissions from the manufacture of the pesticides studied involves wet scrubbing with water. A smaller percentage of plants employ alkali absorption and adsorption processes and filter bags (baghouses). Wet acrubbing, absorption, and adsorption processes are used mainly for controlling gases and vapors, with particulates controlled to a lesser extent. Filter bags are used primarily for controlling particulate emissions.

(6) A factual, realistic assessment of the significance of emissions from pesticides planth is impractical at this time because of the limited quantitative emission data available. This data limitation is compounded by absence of state or Federal source emission standards on which to base such an evaluation. However, in the manufacture of pesticides, there are significant emissions of such compounds as SO_2 , H_2S , and NO_x , and these are substantially higher than emission standards in other related process industries.

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SECTION II

RECOMMENDATIONS

(1) A more effective means of obtaining data than the currently employed method of requesting information by letter from manufacturer needs to be developed. This new means of data collection must simultaneously protect the legitimate proprietary claims of manufacturers, yet insure that EPA and its contractor meet their obligations. Working through an intermediary such as a trade organization may be one of the general strategies needed to accomplish this end.

(2) The air pollution control aspects of the pesticide industry have not been studied as closely as its water pollution control aspects. A detailed study involving air monitoring and sampling at the manufacturing plant and their waste disposal site should be pursued. The author of this report has relied heavily on published data and scanty responses from the pesticide manufacturers. It is recommended that this study be expanded to include plant visits and sampling.

(3) The dearth of field measurements on pesticides emission prevents development of a firm recommendation on source performance standards for the pesticide industry. However, the intrinsic toxicity of intermediate and final products is clear. It is, therefore, recommended that a field emission study be undertaken at the earliest possible date to obtain the data necessary to fully quantie pesticides emission standards.

SECTION 111

INTRODUCTION

Pesticides are important to the nation's economic life because they are used to help in the production of food and fibre and to control organisms that destroy materials or threaten public health. However, the manufacture and use of the pesticides can create environmental and health concerns. Consequently, EPA, through its Office of Pesticide Programs, has engaged in scudies of various aspects of pesticide production, use, and effects on the environment.

Continuing in these important studies, the Strategic Studies Unit of the Office of Pesticides Programs has noted a need to develop background information and determine the significance of the air contaminant emissions from the manufacture of some pesticides, in conformity with the 1970 Clean Air Act that requires the regulatory agencies to gather information and develop standards for emissions from stationary sources. Because there are large numbers of pesticides manufactured in this country, only one or two pesticides from each class were selected for this background study. Six pesticides were selected in total as listed below.

> Insecticides - methyl parathion and toxaphene Herbicide - monosodium methane arsonate (MSMA) and trifluralin Fungicide and wood preservative - pentachlorophenol Fumigant - paradichlorobenzene.

The choice of these specific pesticides by EPA was based on a previous EPA study, which found that the selected pesticides are characterized by high production and use, environmental concerns, regulatory interest, and increased use forecast.^{(1)*}

^{*} References are located on Page 61.

Objectives of the Study

The first general objective of this study has been to develop background information on the manufacture of six pesticides described earlier. Specific objectives have been: (a) to prepare a list of manufacturers in the United States specifying the plant name, location, capacity, and production; (b) to describe the production processes for each pesticide; (c) to describe the emission sources of air contaminants and their control, and estimate the nationwide air contaminant emissions from the plants producing each pesticide; and (d) to prepare a cost estimate of the best available emission control systems and discuss the economic impact on typical firms in the industry if such control were required.

The second general objective has been to determine the severity of air contaminant emissions from the pesticide manufacturing plants and thus identify the need to develop emission standards for such plants.

The Study Approach

The approach centered on the development of background information on the manufacture of six selected mesticides. The study of each pesticide was divided into four tasks as given in Table 1. The table contains the specific information desired on each task.

Data Collection

Information gathering was focused on a literature survey of the manufacture of the six pesticides in the United States. Principal information sources were from BCL in-house data files and government, professional, and trade association publications. Letters requesting data (see Appendices B and C) were sent to 9 manufacturing plants to obtain factual information on various aspects of the selected pesticide manufacture. Information sought included plant capacities and production volumes; processes profiles such as flow sheets, rew and waste materials handling descriptions; source, kind, and

TABLE 1, RESEARCH PLAN

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	Taske	Desired Information
1.	Data Collection	(a) List of Manufacturers
		• Plant name
		• Location
	*	 Capacity
		• Production
		(b) Manufacturing Processes
		Nature of pesticide produced
		 Raw materials
		• Waste materials
		(c) Air Conteminant Emissions
		Control technology
		Level of control
		 Waste disposal involving air
		pollution emission
2.	Process Description	(a) Description of the perturue produced
		(b) Description of raw and waste materials handling
		(c) Manufacturing methods and processes flowsheets
3.	Air Contaminant Emissions and Control	(a) Types and sources of air contaminant emissions
		(b) Types and levels of control
		(c) Estimate of the present emission control situation
		(d) Estimate of future emissions
4.	Gentrol Cost	(a) Estimated cost for best available control
		(b) Economics impact on the industry

quantities of air contaminant emissions, currently applied control methods; and costs of such controls. Several telephone calls were made to the manufacturing plants urging them to complete the forms; however, no plant visits were made.

Process Description

Using the information gathered, flow sheets were developed, and process profiles employed in the manufacture of each pesticide were described. Each flow sheet identified, where possible, the following:

- (1) Steps of manufacturing processes
- (2) Raw materials
- (3) Sources and types of air contaminant emissions
- (4) Waste material disposal methods
- (5) By-producte
- (6) Final and products.

Analysis of Air Contaminant Emission and Control

The air contaminant emissions from the manufacture of each pesticide and the disposal of the wastes were identified and quantified where possible together with the currently employed methods of emission control. The currently employed emission controls were described in terms of gas and particulate removal efficiency ranges, potential reduction of visibility, and odor.

Projections of future emissions were made. By relating these to similar emissions from other sources, a quantitative estimate of the significance of emissions from the manufacturing sector ware made.

The qualitative and quantitative estimates of the present and future nationwide air contaminant emissions from the plants manufacturing each pesticide were based on the plants' capacities and the sir contaminant emissions rates.

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Analysis of Air Contaminant Emission Control Costs

Based on the information obtained from the foregoing tasks, cost estimates were made on the currently employed control methods. The costs consisted of the operating and capital cost estimates. Where possible, and on the basis of available information, cost estimates of the best available emission control systems for a typical firm were made. In addition, a discussion of the economic impact on typical firms in the industry, if such controls were required, was presented.

SECTION IV

BACKGROUND INFORMATION AND SIGNIFICANCE OF AIR CONTAMINANT EMISSIONS

For the convenient presentation of the desired information, the research program outlined in Table 1 was subdivided as follows:

- (1) Production inventory in the United States
- (2) Future production trends
- (3) Manufacturing process
- (4) Raw and waste material handling
- (5) Air contaminant emissions, sources, and rates
- (6) Air contaminant emission control
- (7) Control costa
- (8) Significance of air contaminant emission from the plants.

Available information on the individual pesticide is presented sequencially under the above headings. However, before the discussion, a general look at the manufacturing sites and production quantities is necessary. The manufacturing sites of the selected pesticides are shown in Figure 1. These sites do not include the formulation plant sites but only the active ingredient manufacturing sites.

Quantitative information on the past, present, and future production of the selected pesticides was difficult to obtain. Information on past production was obtained from the U.S. Tariff Commission published data; however, some of these production values are listed in pesticide groups instead of individual pesticides utilized in the program. Present and future production information was sought through the manufacturers, but most failed to give the information for proprietary reasons. Since the past production data did not present a definite trend, an extensive effort was made to forecast production of each pesticide up to 1980. These estimated production data are given in Table 2 and are graphically shown in Figure 2. As will be discussed under each pesticide, a number of factors such as availability of raw materials, demand of the pesticide, and other influences can significantly alter the forecast, so that its reliability decreases as the time interval increases.



FIGURE 1. MANUPACTURING SITES OF THE SELECTED PESTICIDES

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Pesticides	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980
Methyl Parethion (MPT) Production, 10 ⁶ 15.	41.4 ^(a)	$37.2^{(a)}$	51.1 ^(a)	48.9 ^(a)	57	65.6	71.4	81.5	88.0	93.3	98.0
Fercent Growth	~~~~	10 ^(e)	37	4 ^(e)	17	15	13	10	8	6	5
Toxaphene ^(b) Production, 10 ⁶ lbs.	₅₀ (ь)	65 ^(b)	85.1 ^(c)	94.6 ^(c)	108 ^(d)	124.2	142.2	162.8	185.6	207.9	232.9
Percent Crowth		30	31	11	14	15	15	14	14	12	12
Monosodium Methanersonat Production, 10° 16.	e(MSMA) 30.5(a)	24.5 ^(a)	30.7 ^(a)	40.1 ^(a)	50.1	62,6	75.1	90.1	103.6	119.L	131.0
Percent Growth		20 ^(e)	25	31	25	25	20	20	15	15	10
Trifluralin Production, 10 ⁶ lb.	NA	25 ^(a)	21 ^(f)	23.1	25.4	27.9	30.1	32.5	34.5	36.6	38.4
Percent Growth		16 ^(e)	10	10	10	8	8	8	6	6	5
Pentachlorophenol (PCP) Production, 10 ^b lb.	47.2 ^(a)	50.9 ^(a)	49.7 ^(a)	45.6 ⁽²⁾	48.9	51.4	54.5	57.8	61.9	68.1	74.9
Percent Growth		8	2 ^(e)	6 ^(e)	5	5	6	6	ç	10	10
Paradichlorobenze(PDCB) Production, 106 lb.	69.6 ^(a)	70.4 ^(a)	77.3 ^(a)	85.0	93.5	95.4	97.3	99.3	103.3	107.4	111.7
Percent Crewth		1	10	10	10	2	2	2	4	4	4

TABLE 2. PRODUCTION ESTIMATES - 1970 TO 1980

(a) United States Tariff Commission Report-Synthetic Organic Chemicals. (Reference 2)

(b) 55 percent of Toxaphene-Aldrin Group-quoted by U.S. Tariff Commission.

(c) 65 percent of Toxaphene-Aldrin Group-quoted by U.S. Tariff Commission.

(d) 70 percent of Toxaphene-Aldrin Group-quoted by U.S. Tariff Commission.

(e) Indicates percent of decrease in production.

(f) Rümker et al, Reference 1.

.



FIGURE 2. PRODUCTION ESTIMATES (1970-1980) FOR SELECTED PESTICIDES

Insecticide - Methyl Parathion

Methyl parathion is a broad-spectrum organophosphate insecticide. It is highly toxic to humans, a characteristic symptom being the impairment of the nervous system. It is a nonpersistent contact pesticide being used extensively in cotton production. Interest in its use in the production of soyberns and alfalfa is increasing.

Production Inventory

Methyl parathion is manufactured in three southern states: Mississippi, Alabama, and Tennessee. The manufacturing sites are understandably clustered in the major use region--the cotton production belt. The names, location, plant design capacity, and the 1974 estimated production volumes are given in Table 3. Over half of the present production volume is manufactured by Monsanto Company.

The total U. S. capacity for the manufacture of methyl and ethyl parathions [0,0-dimethyl 0-p-nitrophenyl) phosphothioate] is 147 million 1b, but three plants with total capacity of 53 million 1b were not producing methyl parathion in 1974. The 1974 estimated production of methyl parathion is 57 million 1b.

Future Production Trends

Future production will depend on the demand and available raw materials. Major quantities of methyl parathion are exported; hence, foreign demands will undoubtedly influence the volume of production in this country. Increased application of methyl parathion to crops other than cotton also will increase demand. Increased use is being further accelerated by recent world food production demands. An absence of a strong competing pesticide in the marketplace will force an upward trend in production. For example, the recent cancellation of DDT registrations has helped to push upward the production of methyl parathion. A factor that certainly may lower the bulk usage for methyl parathion is the development TABLE 3. PRODUCERS OF METHYL PARATHION IN THE UNITED STATES^(3,4)

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Company	Location	Annual Capacity millions of 15	Estimated 1974 Production millions of 1b
American Cyanamid Company Agricultrual Division	Lindern, N. J.	23	
Hercules Inc. Synthetics Department (a)	Plaquemine, La.	15	
Kerr-McGee Corporation Kerr-McGee Chem. Corp.	Hamilton, Miss.	17	15
Monsanto Company Agricultural Division ^(b)	Anniston, Ala.	50	30
Stauffer Chemical Company (b) Agricultrual Chem. Div.	Mt. Pleasant, Tenn.	30	10
Vicksburg Chemical Company	Vicksburg, Miss.	3	2
Velsicol Chemical Corp.	Bayport, Texas Total	10 153	57

(a) Not operating by 1974.

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(b) Volume includes ethyl parathion.

of a more effective and efficient way of packaging and applying the insecticide, such as encapsulation techniques.⁽⁵⁾

The effect of the foregoing factors on future production of the insecticide is difficult to predict. However, responding industries estimated that the annual rate of increase in production will decline from the 1973-1974 level of about 17 percent to about 5.0 percent by the year 1980. On this basis, 1980 production will be about 98.0 million pounds.

Manufacturing Process

Methyl parathion is commonly manufactured from sodium p-nitrophenolate by the reaction with 0,0-dimethyl phosphorothiochloridate. There are three steps involved in the synthesis of methyl parathion. One common method involves the reaction of an appropriate alcohol (methyl alcohol) with phosphorus pentasulfide, followed by chlorination, and finally, the parathion formation in acetone. The three steps are as follows:



Conditions of these reactions are not available as they are proprietary.

Raw and Waste Material Handling

The raw materials are sodium p-nitrophenolate, methyl alcohol, chlorine, and phosphorous pentasulfide. In the production of methyl parathion, by-products such as NaCl and HCl are formed along with waste products such as H_2S , mercaptan, and sulfur. The production and waste

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FIGURE 3. PRODUCTION AND WASTE HANDLING SCHEMATIC FOR METHYL PARATHION (Monsanto)⁽⁶⁾

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handling schematic is shown in Figure 3. The odorous compounds (H_2S and mercaptan) are flared and the sulfur is incinerated, while liquid waste effluents are neutralized with Na_2CO_3 and sent to a wastewater treatment plant.

Since methyl parathion is very toxic, specific handling precautions are taken. Karr-McGee Corporation provides the following precautionary steps in their plant:

- (1) Raw materials except for SNP (sodium p-nitrophenolate) are stored in tanks located in diked areas or in submerged sumps. SNP is stored in powder form out of doors. The SNP is stored in reconditioned, open head type, bolted top ring drums. Drainage from the SNP drum storage area is to the chemical complex drainage ditches.
- (2) Processing areas of the plant are curbed so that spills, gland water from pumps, and contaminated runoff are contained and treated as process wastewater.
- (3) Liquid parathion is stored in a new roofed warehouse that does not drain or discharge into any wastewater effluent systems. The parathion is stored in 16 gauge, tight head drums. In the event of a parathion spill the following clean-up steps are taken in the order listed:
 - Put absorbent clay on the spill until the spill is soaked up in the clay.
 - . Remove the clay and absorbed parathion.
 - Put soda ash over the spill area. Vigorously scrub soda ash into floor with a broom.
 - Remove soda ash.
 - Repeat Steps 3 and 4 several times.
 - Wipe contaminated area with paper towel.
 - Soak paper towel in carbon disulfide to extract methyl parathion.
 - Check carbon disulfide for methyl parathion by infrared scan.

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- If the test is positive repeat Steps 3 through 8 until the test is negative.
- Bury contaminated matter in closed drum.

Air Contaminant Emissions, Sources, and Rates

The manufacture of methyl parathion produces solid, liquid, and gaseous waste materials.

The main sources of air contaminant emissions are: the reactor, the chlorinator, and the Methyl Parathion unit (Figure 3). Odorous pollutants arise from vents, liquid wastes, and residues. During the disposal of by-products (for example, flaring of H_2S and mercaptans and incineration of sulfur), sulfur dioxide is given off. Also, during wastewater treatment or lagooning, the odorous compounds such as H_2S , mercaptans, acc., are emitted.

The companies contacted were unable to furnish any data on the rate of air pollutant emissions from their plants. Emission rates for H_2S , S, and NaCl were calculated as 460, 420, and 460 pounds per hour, respectively, on the basis of 330 days per year and a 24-hour-per-day operation.* Sulfur dioxide emission rates based on H_2S and S oxidation are estimated to be 1,550 pounds per hour from the following reactions:

 $2H_2S + 3O_3 \longrightarrow 2SO_2 + 2H_2O$ $S + O_2 \longrightarrow SO_2$.

The air emission sources, compounds, and rates are given in Table 4.

Air Contaminant Emission Control

Air contaminants arising from the production processes are controlled by the methods used in general chemical industries to prevent dusts, fumes, and gases from leaving the production plant into the outside environment.

These calculations are based on an annual production of 30×10^6 pounds of methyl parathion and the estimates by Rawless, et al. (6)

Sources of Emission	Particulates	Rates, lb/hr	Gas es/Vapor s	Rates, lb/hr	Od or	Rate, Odor Unit/h :
Manufacturing Processes		_				
Reactor	None		diphosphorus pentoxide mercaptan H ₂ S		mercaptan kvlene H ₂ S	
Chlorination	Acid Mist. e.g. HCl S	460 420	PCl ₃ PSCl ₃ Methanol Methyl chloride HCl			
MPT Unit	Basic Mist, e.g. NaCl Methyl Mono- chloride	460				
Maste Treatment Processes	3					
Incinerator and Flaring	P2 ⁰ 5		so, P205	1,550	Non	
Waste Treatment Plant	None		H ₂ S mercaptan		H ₂ S mercaptan	
Lagooning	None		H ₂ S mercaptan		H ₂ S mercaptan	

TABLE 4. AIR CONTAMINANT EMISSIONS, SOURCES, AND RATES FROM METHYL PARATHION MANUFACTURE AND WASTE TREATMENT

Practical sulfur dioxide emission control processes for H₂S, mercaptun, etc., available for methyl parathion plants are incineration in series with scrubbing system and carbon adsorption. Control of visible fumes created by the emission of diphosphorous pentoxide can be achieved by a mist eliminator, while H₂S and mercaptan emission control during the wastewater treatment can be achieved by chemical oxidation and deodorization.

The air emission control system used by Monsanto is shown in Figure 4. Incineration is used for the control of the off gases and residue, while heavy chlorination is used for the control of the wastewater odorous emissions. The scrubbing system used to control the incinerator emission is quoted to achieve an efficiency of 95 percent for the removal of diphosphorous pentoxide. The Brink Mist Eliminator provides about 99.9 percent visibilit, reduction. Incineration of sulfur may be considered a better practical control method than recovery because the sulfur that can be recovered in this process is inescapably contaminated with toxic methyl parathion.



Sulfur dioxide emissions presently are not controlled in methyl parathion manufacturing plants. This means that for a plant producing about 30 million 1b of methyl parathion per year, the SO₂ emission per year will be about 12.3 million 1b or 1,550 lb per hour; that is, by 1980 at the present control status SO₂ emission from MPT plants will be about 21.2 million 1b or 2,680 1b per hour. On the basis of available information, Monsanto is the only company manufacturing methyl parathion that is controlling air emissions; the sulfur compounds by incineration, diphosphorous pentoxide by scrubbing, and visibility by the Brink Mist Eliminator. However, SO_2 produced during the incineration of sulfur compounds is not controlled. It was estimated that about 12.3 million 1b of SO_2 were emitted in 1974. Both Kerr-McGee Corporation and Stauffer Chemical Company vent their emission into the atmosphere without any control. According to them, there are occasional complaints of odor problems from H_2S , mercaptan, etc., emissions. It was estimated that H_2S , S, and NaCl emissions from these plants were, respectively, 3.2, 3.0, and 3.2 million 1b in 1974.

The future trend in air pollution from the manufacture of methyl parathion will tend to increase due to increased future production unless efforts are made to control the emissions. Large manufacturing companies, such as Monsanto, tend to be able to install control equipment, but the smaller companies indicated that control was economically unfeasible.

Control Costs

Monsanto declined to provide its air pollution control costs. Estimation of the control costs by theoretical calculations are not possible within the resources allotted for this study.

Significance of Air Contaminant Emission

The present emission control situation in the manufacture of methyl parathion shows that only Monsanco Company controls the primary emissions such as H_2S , mercaptan, S, and phosphorous pentoxide, while other companies do not control their emissions. However, in the process of controlling the primary emissions, a secondary emission (SO₂) is produced and emitted without control.

Those companies that are not controling H_2S and mercaptan emissions do have occasional odor problems; here, control in the industry is necessary. Kraft pulp mills may be compared with the methyl parathion plant in terms of odor problems. The emission requirement in Mississippi and Alabama for the total reduced sulfur (TRS) is 1.2 and 2.0 ib/ton of pulp, respectively;^(B) whereas the calculated emission for H₂S alone from the methyl parathion plant was about 0.12 lb/lb of active ingredient (AI). Also, SO₂ emission standard from sulfur recovery plants may be compared with that emitted at the Monsanto plant. In Alabama, the standard is 0.08 lb/lb of sulfur processed, while the calculated emission from the Monsanto plant was about 0.41 lb/lb of AI. Consequently, these odorous compounds and SO₂ are emitted in an amount higher than prevailing state standards for other related process plants. Thus, the need for control of these emissions from the methyl parathion plant is significant.

The economic impact of controlling these pollutants is not assessed since the control costs were not available.

Insecticide - Toxaphene

Toxaphene, a nondefinite chemical compound, is a mixture of polychloro-bicyclic rerpenes with chlorinated camphene. Toxaphene contains 67 to 69 percent chlorine.

Toxaphene is less persistent in the environment compared with the other compounds in this general group, e.g., aldrin, dieldrin, and endrin. Toxaphene is severely toxic to aquatic ecosystems, especially to fishes. It is also toxic to terrestrial ecosystems, but the effects are less widespread than those caused by the more persistent chlorinated hydrocarbon pesticides. (1)

Toxaphene is an important agricultural insectionde, especially in preventing cotton plant damage. It is normally applicable against the boll weevil, boll worm, cotton aphid, and cotton fles hopper.

Production Inventory

Toxaphene is manufactured in three southern states; namely, Georgia, Texas, and Missouri, and by three companies, namely, Hercules, Sanford, and Vicksburg. Table 5 gives the inventory in the United States.

Company	Location	Design Capacity	Production Estimate 1974
Hercules, Inc. Synthetics Dept.	Brunswick, Ga.	50-75 ^(b)	65
Sonford Chemical Co.	Houston, Tex.	40	20
Tenneco Chemicals Intermediates Div.	Fords, N. J. ^(a)	125 ^(b)	20
Vicksburg Chemical Co.	Vicksburg, Miss.	5	3
		220-245	108

TABLE 5. PRODUCERS OF TOXAPHENE IN THE UNITED STATES (3)

(a) Produces strobane, a polychlorinated toxaphene-like insecticide.

(b) Reference 1.

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The distribution conforms with the general location of raw material-southern pine--and major use area--the southern cotton fields.

The plant capacities and production volume for toxaphene are difficult to estimate reliably. The firms contacted would not furnish the information. Also, the U.S. Tariff Commission does not report separately on toxaphene, but instead, as the aldrin-toxaphene group which contains compounds: aldrin, chlordane, endrin, dieldrin, heptachlor, strobane, and toxaphene. The production of this shole group showed a dramatic increase from 1970 to 1972. The U.S. production of toxaphene was estimated to be 50 million 1b in 1970.⁽²⁾ An estimate discussed below for 1974 is 108 million 1b, showing that the production has substantially increased.

Future Production Trends

Estimates of toxaphene production are based on the trend in the proportion of toxaphene in the aldrin-toxaphene group. In 1970, toxaphene was about 55 percent of the group production.⁽²⁾ In 1973, it was about 65 percent, and with the recent registration withdrawal of some insecticides of this group by EPA, such as aldrin, endrin, and dieldrin, the proportion and, hence, the production of toxaphene is expected to increase.

Increases in agricultural production will provide an upward trend in production. However, like methyl parathion, new, more efficient, and effective methods of packaging and application will tend to lower demands.⁽⁵⁾

On the basis of these factors, the percentage of increase in production of toxaphene will tend to decrease from the present estimated rate of about 25 percent to about 12 percent by the year 1980, giving a production volume of 233.0 million 1b per year at the end of the decade as shown in Table 2. The above estimates have been made on the assumption that no regulacory action will be taken to control the use of toxaphene or that no substitute chemicals will be introduced.
Manufacturing Process

The production of toxaphene involves two main steps: the production of camphene in a reactor from α -pinene, which is a compound obtained from southern pine stumps; and the reaction of chlorine gas with camphene in a solvent solution at the chlorinator.

The reaction chemistry is given below. (6)



o-Pinene

Camphene

Toxaphene (mixed isomers and related compounds 67-69% Cl)

Details of the operating conditions in the manufacture are not available since they are proprietery.

Kaw and Waste Moterial Handling

The raw materials involved in the manufacture of toxaphene are camphene, chlorine, and solvent, plus other compounds used in the effluent treatments.

The production and waste material handling schematic used by Hercules is presented in Figure 5. The gaseous emissions from the chlorinator, chlorine gas, hydrochloric acid, and solvent vapors are passed through condensers, caustic scrubbers, and a tower containing limestone, while the liquid toxaphene is filtered, stripped, and formulated into marketable forms. The wastewater is neutralized and subjected to primary treatment prior to discharge to the creek.

Herculas claims to have rigorous safety standards. They maintain a fire truck and crew on site. Production workers receive annual checkups and have had on excellent health record, according to the company, with no



FIGURE 5. PRODUCTION AND WASTE HANDLING SCHEMATIC FOR TOXAPHENE⁽⁶⁾

correlations of death or illness with toxaphene handling. The company stated that they are in compliance with all air pollution control regulations promulgated by the State of Georgia under the Federal Clean Air Act of 1970. Information on raw and waste material handling at other manufacturing plants is not available.

Air Contaminant Emissions, Sources, and Races

Main sources of air contaminant emissions are the reactor, the chlorinator, and toxaphene formulations. There is no information on emissions from α -pinene production.

The main emission from the reactor is chlorine gas; the emissions from the chlorinator are chlorine gas, hydrochloric acid, and solvent vapor, and toxaphene particulates are released during formulation. These compounds and sources are given in Table 6. The emission rates of these compounds are not available, except HCl which is estimated to be 4,350 lb/hr* from a 65-million-lb-capacity plant.

Air Contaminant Emission Control

Most systems available in chemical industries for controlling acidic gases are applicable to the control of emissions from the manufacture of toxaphene. There are three main control techniques: scrubbing (alkali or water), stripping and adsorption.

Hercules uses these control techniques to control HCl, chlorine gas, and solvent vapor emissions. The emissions are initially passed through condensers where the majority of the solvent and hydrochloric acid is removed. Following the condensers are caustic scrubbers which remove additional traces of hydrochloric acid and chlorine. Finally, the effluent is passed through large towers containing limestone, which is said to remove the "balance" of the hydrochloric acid. The final rate of emissions from the limestone towers is not known, but Hercules claims up to 100 percent efficiency.

* Estimated at 0.53 lb/lb AI.⁽⁶⁾

Sourc	es of Emission	Particulates	Rate, lb/hr	Gases/ Vapors	Rate, lb/hr	Odor	Rate, Odor "nits/hr
Manuf	acturing Steps						
	∂ -Pinene Production	NA		NA		NA	
	Camphene-Production (Reactor)	NA		NA		NA	
	Chlorination-Toxaphene Production	None		Cl ₂ gas HCl Solvent Vapor	4350 ⁽⁶⁾	NA	
	Toxaphene Granular Production	Toxaphene Dust		None		None	
Waste	Treatment Processes						
Was	tewater Treatment Plant	None		С1 ₂ нс1		Possible candidat ^{C1} 2	 c

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TABLE 6. AIR CONTAMINANT EMISSIONS, SOURCES, AND RATES FROM TOXAPHENE MANUFACTURE AND WASTE TREATMENT

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In chemical industries various control technologies are available for controlling particulates, such as electrostatic precipitators, baghouses, scrubbers, etc.

Hercules uses baghouses to control the toxaphene particulate emissions. No information is available on the uncontrolled and controlled emissions.

No definite statement can be made on the present air pollution control status in the manufacture of toxaphene. Control information is unavailable from other manufacturing plants.

Control Costs

Emissions from the manufacture of toxaphene are not controlled separately; instead, they are passed together with emissions from the manufacture of other pesticides in their class through the same control system. Consequently, control cost information is unavailable.

Significance of Air Contaminant Emission

There is high emission of HCl (about 0.53 lb/lb AI) in the manufacture of toxaphene. It is recognized that HCl is a liquid at normal temperature and pressure. However, fumes of HCl are emitted, although the rate of emission is not known.

A particularly important emission in the manufacture of toxaphene is that of toxaphene particulates. Toxaphene is toxic to mammals; for example, the toxic level for dogs is 20 ppm.⁽¹⁾ However, data are unavailable on the rate of emission from any plant. Consequently, an assessment of the significance of emission from the plants is not possible at this time.

Herbicide - Monosodium Acid Methanearsonate (MSMA)

MSMA is a selective herbicide of the organic arsenical group. MSMA is not very toxic to animals and it degrades fairly readily in the soil. It is a postemergent herbicide used to control hard-to-kill grass weeds.

Production Inventory

Monosodium acid methanearsonate is produced in three states--Wisconsin, Texas, and New Jersey--and by three companies--The Ansul Company, Diamond Shamrock Chemical Company, and Vineland Chemical Company. The plant design capacities of the producers and their production are shown in Table 7.

The U. S. capacities and production volumes are known for the Ansul Company and Diamond Shamrock Chemical Company. Their combined estimated production for 1973 and 1974 were 33.1 and 32.4 million 1b, respectively. No information is available on the capacity and production volume of Vineland Chemical Company. However, it is estimated that the total production for the methanearsonic acid salts for 1973 and 1974 is about 40 to 50 million 1b, respectively.

Future Production Trends

The production of MSMA has been showing an upward trend since 1971. Ansul has been producing at design capacity while Diamond Shamrock Chemical Company has maintained a production of about 50 percent above design capacity. This means that either new plants will be built or existing ones expanded, or both, to meet the demand. MSMA belongs to the organic derivatives of the trivalent form of arsenic. Its selective, postemergent efficacy against hard-to-kill grass weeds makes MSMA an important herbicide in agricultural production. Therefore, its production in years ahead will tend to increase with the recent increased demand in the production of food and fibre. The appearance of competing herbicide in the marketplace may lower the production of MSMA.

A conservative estimate for the production has been presented in Table 1. Again, an increase in production is projected, but this rate of increase will tend to decrease from the present 25 percent annually to about 10 percent annually by the year 1980.

		Design Plant Capacity	Production Estimate million 1b		
Company	Location	million 1b	1973	1974	
The Ansul Co., Chemical Div.	Marinette, Wisc.	10	16.1	15.7	
Diamond Shamrock Chemical Co., Agricultural Div.	Greens Bayo, Tex.	17	17.0	16.7	
Vineland Chemical Co.	Vineland, N. J.		NA	NA	

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TABLE 7. PRODUCERS OF MSMA IN THE UNITED STATES (3)

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Manufacturing Process

Three main steps are involved in the manufacture of MSMA: production of sodium arsenite, methylarsonic acid, and MSMA.

The first step in the production of MSMA begins with the formation of sodium arsenite by the reaction of arsenic trioxide and 50 percent caustic soda solution. In the next step, 25 percent solution of the sodium arsenite is treated under pressure with methyl chloride to give the disodium methane arsenate (DSMA). Some companies sell a portion of the DSMA for herbicide uses, but since DSMA is less soluble, it requires a higher application rate. Most companies go a step further to prepare MSMA.

MSMA is prepared by adjusting the pH of DSMA with sulfuric acid in a reactor. The material is centrifuged to remove salts such as sodium sulfate and sodium chloride (which are waste by-products) and the resulting solution is concentrated by evaporating the water. Hydrogen peroxide is added to oxidize the unreacted trivalent arsenic to the pentavalent form. The final product is formulated with a wetting agent and packaged into 1-gallon, 5-gallon, 30-gallor, or 55-gallon containers. The active ingredient of MSMA is sold at a number of concentrations, but approximately 58 percent is the maximum concentration that can be prepared without undue viscosity effects.

The simple process chemistry is given below.

 $As_{2}O_{3} + 6NaOH \longrightarrow 2Na_{3}AsO_{3} + 3H_{2}O$ Arsenic Sodium
Trioxide Arsenite $Na_{3}AsO_{3} + CH_{3}C1 \longrightarrow CH_{3}AsO(ONa)_{2} + NaC1$ Methyl DMSA
Chloride $2CH_{3}AsO(ONa)_{2} + H_{2}SO_{4} \longrightarrow 2CH_{3}As \bigcirc ONa + Na_{2}SO_{4}$ DSMA MSMA

Raw and Waste Material Handling

Raw materials used to produce MSMA are argenic trioxide, sodium hydroxide, methyl chloride, and sulfuric acid. Arsenic trioxide is the most toxic species, and it is imperative that this compound be handled with care.

It is unloaded under a hood equipped with an exhaust blower that pulls the dest through ducts to a dust collector, or scrubber. Employees use respirators, and frequent employee health screening to check any health donger is required by most firms.

The production and waste schematic (6) is shown in Figure 6.

A major concern in the wastewater treatment is the disposal of the mixture of sodium sulfate and sodium chlorate contaminated with arsenic. Diamond Shamrock handles this by precipitation and centrifugation. After washing, they are disposed of in a landfill which is registered with the State of Texas. No information on air emissions from the disposal site is available. Methanol, a side product of methyl chloride hydrolysis and water, is recycled.

Air Contaminant Emissions, Sources, and Rates

The main source of air contaminant emissions during the manufacture of MSMA is in the sodium arsenite production during the unleading of arsenic trioxide. Minor emissions may occur during the processing of the MSMA by evaporation from vents of the reactors.

The main emission during the production of sodium arsenite is arsenic trioxide, which is very toxic. Diamond estimates the controlled emission of As_2O_3 to be 6 x 10^{-8} lb/ton or 6.44 x 10^{-8} lb/hr. During the production of DMSA and MSMA, vapors of CH₃Cl, Na₂SO₄, and CH₃O₄ are given off.

Arsenic-contaminated solid materials including NaCl, Na₂SO₄, and MSMA are landfilled. No information is available on the emissions from these disposal sites. The list of the pollutants from various sources is given in Table 8.



Sources of Emissions	Particulates	Rates, 1b/hr	Gases/ Vapors	Rates, 1b/hr	Odor	Rates, Odor Unit/hr
Manufacturing Steps					-	
Sodium Hearton (Reactor Vents)	As203	6.44x10 ⁻⁸				
DMSA Production (Reactor Vents)	None		сн ₃ с1 сн ₃ он (сн ₃) ₂ о		Same	
MSMA Production (Reactor Vents)	None		NaC1 N ₂ SO ₄ MSMA	••	Samc	
MSMA Processing (Evaporator and Centrifuge)	MSMA					
Waste Disposal Processes						
Landfill	NA		Not Identified		Not Identif	ied
Ponds	NA		11			

TABLE 8. AIR CONTAMINANT EMISSIONS, SOURCES AND RATES FROM MSMA MANUFACTURE AND WASTE TREATMENT

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Air Contaminant Emission Control

The only air pollutant controlled in this industry is As₂O₃. The compound is emitted as particulates and various control techniques are available, such as baghouses, scrubbers, and electrostatic precipitators.

Diamond Shamrock operates the As_2O_3 drum opening and dump bin under a hood equipped with a blower that will pull the As_2O_2 into a bagfilter for collection. Ansul's plant controls the arsenic trioxide emission by a scrubbing system. Efficiencies of these control systems are not known by the firms. The best control technique for this highly toxic arsenic trioxide is to have both baghouses and acrubbers in series. The bag filter is useful in recovering As_2O_3 , while the scrubber removes the smaller size particles that normally will not be collected by the bag filter. Unfortunately, the scrubbing system may create water pollution problems.

Assuming an industry estimate of a controlled emission rate of 6.44×10^{-8} lb/hr As₂O₃, it is estimated that the amount emitted per year by a plant of 17 million lb capacity is 5.1×10^{-4} lb.

Ansul Company observed occasional odor nuisance, but no identification of the odor-producing compounds has been made.

A definite statement on the level of emission control is not possible because of incomplete data. However, it can safely be stated that all companies control arsenic trioxide emission but controlled emission rates are not known. A definite need exists to monitor the emission of this very toxic pollutant.

Future emissions will increase on the order of the production projections if the present level of control is maintained. Assuming an emission rate of As_2O_3 given by Diamond Company as 6.44 x 10^{-8} lb/hr As_2O_3 emission for the industry by 1980 will be 0.0393 lb/year.

Control Costs

Diamond Shamrock--with design capacity of 17 million 1b per year-gives the cost for controlling As_2O_3 as \$8,000 for capital cost, and \$200 per year for the operating costs. An acidifier vent scrubber is said to

cost \$500 for the capital, and \$100 per year as the operating cost. Air flow rates and hence sizes and efficiencies of the equipment were not provided for verification purposes.

Significance of Air Contaminant Emission

Of importance in the industry is the control of As_2O_3 emissions because of their high toxicity and carcinogenic property. As of this date, the responding firms do control As_2O_3 emissions but the level of control is not known.

Herbicide - Trifluralin

Trifluralin is a selective soil-applied or preemergence herbicide of the class Nitroaromatic. It is used to control annual grass weeds and some annual broad-leaves. About 60 percent of the trifluralin is used in the production of soybeans, 30 percent cotton, and 10 percent others. (1)

Toxicity of trifluralin to mammals is low, but it is highly toxic to fish. It is degradable by microbial activity, and moderately persistent in the soil, with about 85 percent of the applied rate degrading during the growing season.⁽¹⁾

Production Inventory

Trifluralin is manufactured by only one firm, Eli Lilly and Company, at their Tippecanoe Labs at Lafayette, Indiana. The plant capacity is estimated to be 35 million pounds per year. Production volumes for 1971 and 1972 were estimated respectively as 25 and 21 million pounds.

Future Production Trends

The future production of trifluralin will depend on availability of raw materials and sale of trifluralin. The impact of the availability of raw materials on trifluralin production is difficult to assess because of many unpredictable influencing factors.

Since trifluralin is mainly used in agricultural production such as cotton, soybeans, etc., the future growth rate of these crops will influence the growth in production of trifluralin.

The production of these crops in the years shead will increase because of the current demand in agricultural production.

In the projections given in Table 1, increased agricultural production was reflected in increased trifluralin production while the appearance of potential competing herbicides was reflected in a decreased percentage of growth. By 1980, it is projected that about 38 million pounds will be produced.

Manufacturing Process

The manufacture of trifluralin involves two main steps: nitration and amination. The simple process chemistry is given below while the flow diagram is shown in Figure 7.



Nitration involves the reaction of the following compounds in reactors: p-chlorobenzotrifluoride, sulfuric acid, and nitric acid. The product of the reaction is 3,5-dinitro-4-chlorobenzotrifluoride, and the by-product is spent sulfuric acid which is recycled. The main off-gases are nitrogen oxides.

Amination is the second-stage reaction involving the reaction of 3,5-dinitro-4-chlorobenzotrifluoride, dipropyl smine, and sodium carbonate in solution. The product of the reaction is triflurslin and the effluent is brine solution which is treated for recovery.



FIGURE 7. SIMPLE FLOWSHELT FOR TRIFLURALIN MANUPACTURE

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Raw and Waste Material Handling

The raw materials used in the manufacture of trifluralin are nitric acid, sulfuric acid, sodium carbonate, dipropylamine, and p-chlorobenzotrifluoride. The main toxic materials are the acida, and their handling practices in chemical industries are well-known.

Eli Lilly provided information of the measures adopted to protect the nealth of their employees. There included wearing protective clothing including self-contained breathing apparatus for certain unloading operations, isolation piping and tanks for each raw material, containment procedures and facilities for accidental spills, routine review procedures between operators, and safety and material handling personnel.

Greater detail of the production and waste handling schematic is shown in Figure 8.

Air Contaminant Emissions, Sources, and Rates

The main sources of air contaminant emissions are the nitration reactor and condenser.

The main gaseous emissions from the nitration reactor are sulfur dioxide, sulfur trioxide, hydrogen fluoride, hydrogen chloride, and nitrogen oxides, while particulate emissions from the reactor consist of nitrate, sulfate, and chloride. Emissions from the condensers are mainly aerosol consisting of trichloromethane and trifluralin. The wastewater from the plant is neutralized, and subjected to the conven ional waste treatment of primary clarification and secondary aerated biological treatment. There are no odors or other air contaminant emissions during the wastewater treatment. Table 9 is a list of the contaminants emitted and their rates as measured by the company.



FIGURE 8. PRODUCTION AND WASTE HANDLING SCHEMATIC FOR TRIFLURALIN(6)

Sources	Particulates	Rate, 15/hr	Gases/Vapors	Rate, lb/hr	Odor	Rate, Odor Unit/hr
Manufacturing Process						
Nitration	nitrate sulfate chloride	1 1 1	sulfur dioxide sulfur tioxide hydrogen fluoride hydrogen chloride nitrogen oxides	3 1 1 10 3	None	
Condenser	CHCl3 Trifluralin	NA NA			None	
Wastewater Treatment	None		None			

TABLE 9. AIR CONTAMINANT EMISSIONS, SOJRCES, AND RATES FROM TRIFLURALIN MANUFACTURE AND WASTE TREATMENT

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Air Contaminant Emission Control

Air contaminant emissions from the manufacture of trifluralin are primarily gases and particulates. Control of these compounds in the chemical industry is achieved by many methods, but those directly applicable to the trifluralin industry are wet scrubbers.

Eli Lilly uses wet scrubbers and their quoted efficiency is about 90 percent.

Control Costs

The Eli Lilly emission control system consists of 1- and 2-stage venturi scrubbers and tri-mer wet scrubbers. The total flow through the system is about 20,000 standard cubic feet per minute. Eli Lilly estimates that capital cost so far is about one million dollars. They have no information on the operating cost.

Significance of Air Contaminant Emission

There are a large number of air contaminant emissions in the industry. The State of Indiana has no stationary source emission standard for sulfur and nitrogen compounds from the process industry. However, the emission rates of these compounds are small when compared with the State of Massachusetts standards which are 10 lb/hr for nitrogen oxides and 25 lb/hr for the process industry which are 10 lb/hr for nitrogen oxides and 25 lb/hr for sulfur exide.⁽⁸⁾ The toxic material emitted to the environment is trifluralin which, according to present knowledge, is highly toxic only to fish and not to mammals. Unfortunately, data are not available on emission rates.

Fungicide and Wood Preservation - Pentachlorophenol

Pentachlorophenol (PCP) is a wood preservative, but it is also used as a contact herbicide. About 75 percent of the PCP is used as a wood preservative for poles, crossarms, and pilings. It is hazardous to man primarily because it is capable of causing eye injuries such as conjunctival redness, iritis, and slight corneal damage. In solution, it can be absorbed through the skin to toxic amounts. Consequently, its handling requires due precautions.

PCP is biodegradable and thus gives no long-term pollution problems.

Production Inventory

Pentachlorophenol is manufactured at five chemical companier in five states. Unlike some agricultural pesticides, which are restricted to the area of intense application, it is not restricted to one geographical area. Because of its wide application in the field of industrial preservation, and logistics of distribution, it is produced in states widely separated -- Washington, Kansas, Texas, Michigan, and Illinois.

The present annual U.S. capacity for the manufacture of PCP is about 97 million pounds. In 1973, the production was 46.6 million pounds⁽³⁾ and the estimate for 1974 is about 48.9 million pounds. The manufacturers of PCP, their capacities, and estimated production for 1974 are shown in Table 10.

Future Production Trends

With the increased cost of other wood preservatives such as crude oil and coal tar crudes (creosote), the demand for PCP as a wood preservative may increase.

However, since PCP is used almost exclusively as a wood preservative for power and phone transmission poles, the increasing use of underground transmission and nonwood-related materials for poles, such as concrete and glass fibre, will tend to force PCP to peak about 1980 and then diminish. Production projections to 1980 are given in Table J. A gradual increase in production is forecast from the present 5 percent to 10 percent by 1980. The greatest impetua to production appears to be the lack of a competing product like crude oil, which is supported by the

Compeny	Location	Annual Capacity, million lb	Est. 1974 Production, million lb
Dow Chemical Co.	Midlanj, Michigan	18	5
Monsanto Indist, Chems, Co.	Sauget, Illinois	26	10
Reichhold Chems., Inc.	Tacoma, Washington	16	10
Sonford Chemical Co.	Houston, Texas	18	5.2
Vulcan Materials Co.	Wichita, Kansas	19	18.7
Chemicals Division	Total	97	48.9

TABLE 10. PRODUCERS OF PCP IN THE UNITED STATES (3,9)

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estimates of some of the companies who think that their production will double by 1980. The projected 1980 production is 74.3 million pounds.

Manufacturing Process

Almost all of the PCF produced in the United States is manufactured by the chlorination of phenol. A simple reaction chemistry of the process is shown below; and the simple schematic in Figure 9.





FIGURE 9. PRODUCTION AND WASTE HANDLING SCHEMATIC FOR PENTACHLOROPHENOL (10)

The general manufacturing process can be described as follows. ⁽¹⁰⁾ The chlorination is performed at substantially atmospheric pressure in a reactor. The temperature of the phenol in the primary reactor at the start is in the range of 65-130°C (preferably 105°C) and is held in the cange until the melting point of the product reaches 95°C. About three or four atoms of chlorine are combined at this point, and the temperature is progressively increased to maintain a temperature of about 10°C over the product melting point, until the reaction is completed in 5-15 hours. The mixture is a liquid, and a solvent is not required, but the catalyst concentration is critical; about 0.0075 mole of anhydrous aluminum chloride is usually used per mole of phenol.

he PCP from the reactions may be further treated (formulated) to effect more marketable products. At Reichhold, the PCP undergoes ingot casting and shotting operation.

Rew and Waste Material Handling

The raw materials used in the manufacture of PCP are phenol, chlorine, and a catalyst -- aluminum chloride. Sources of raw materials vary from firm to firm. Some manufacturers produce these materials on site, while others purchase the same.

Dow Chemical makes phenol from benzene (via monochiomobenzene), but this method of making phenol is being generally replaced by the cumene oxidation process. Monsanto also makes both the phenol and chlorine; while Vulcan makes the chlorine, but purchases the phenol; and Reichhold makes the phenol, but purchases the chlorine.

While some companies report that no particular precautions are taken at PCP plants, others point out specific precautions such as handling chlorine and phenol in closed systems, and the use of plant coveralls, rubber gloves, safety glasses, goggles, and hard hats. There are occasional face shields and respirators for employee protection when the situation calls for their use.

Air Contaminant Emissions, Sources, and Rates

In the manufacture of pentachlorophenol, there are three main sources of air emissions: the PCP reactor, ingot and shotting operation, and the acid system reactors. At the PCP reactor, the following compounds are emitted: chlorine gas, hydrochloric acid vapor (HCl), and chlorinated phenols. At the acid system reactors and process vents the chlorinated phenol and chlorine are emitted. The particulate emission from the manufacturing process is limited to PCP dust from the ingot casting and shotting operation.

There are no air contaminant emissions reported from the wastewater treatment. The sources of emissions and pollutants are given in Table 11.

Air Contaminant Emission Control

Major emissions from the manufacture of PCP are gases and particulates, which are amenable to chemical industrial air pollution control techniques. Practical controls used in the industry are scrubbers for the gaseous emissions, and filter bags for the particulates.

Reichhold by-product recovery systems and air pollution control systems for gaseous and particulate emissions are shown in Figures 10 and 11, respectively. The control methods in terms of efficiencies are described in Table 12.

Firms responding to our questionnaires reported that under proper operation of these control devices, exhaust effluents are invisible and free from odor.

Cost of Control

Reichhold gave the following control costs for their 12-millionpound-capacity plant:

Sources of Emission	Particulates	Rates, lb/hr	Gases/Vapors	Rates, !b/hr	Odor	Rates, Odor Units/hr
Manufacturing Process						
PCP Reactor	None		 (1) chlorinated phenol (2) chlorine gas (3) Hydrochloric acid vapor 			
Acid System Reactors	None		 (1) chlorinated phenol (2) chlorine gas (3) Hydrochloric acid vapor 			
Ingot Casting	PCP		None		PCP	
Shotting Operation	PCP		None		PCP	
Wascewater Treatment					None	

TABLE 11. AIR CONTAMINANT EMISSIONS, SOURCES, AND RATES FROM PCP MANUFACTURE AND WASTE TREATMENT

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FIGURE 10. SCRUBBING SYSTEMS FOR THE CONTROL OF HC1, C1 EMITTED FROM PCP REACTOR

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FIGURE 11. DUST COLLECTOR SCHEMATICS FOR THE PENTA EMISSION CONTROL

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Control System	Efficiency, percent	Compound Controlled	Controlled Emission, 1b/ton
Wet Packed and Venturi Scrubber (with water)	99-100	Cl2 HCl Phenol Sodium Penta- chloro phenato	N.A. N.A. 2 =/ 4.32 =/
Dust Collector (bay filters) at ingot casting	99	PCP Fume	0.1 <u>b</u> /
at shotting operation	95	PCP	1 <u>b</u> /

 TABLE
 12.
 AIR CONTAMINANT CONTROL METHODS

 USED
 IN PCP MANUFACTURE

(a) Controlled emission reported by Monsanto based on 1974 production.

(b) Controlled emission reported by Reichhold based on 1974 production.

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Name of Con	utrol Device	<u>.</u>	<u>Size</u>	Capital Cost(\$)	Operating <u>Cost (\$/yr)</u>
Bag filter	(2)	(1) 2	2000 ft 2*	\$ 70,000	\$ 6,000
		(2)	450 ft^2		
Mechanical Seals (for FCP reactor)			50,000	6,250	
Phenol and	Acid Scrubber			80,000	1,000

[#]Area of bag filter.

According to Reichhold, the greatest problem arose from the dust collectors because of the lack of reliability. They consider dust emissions less than the present 1.0 lb/ton to be too restrictive, since this will require additional capital expenditures in excess of \$100,000 and operating costs of \$10,000/year for their plant capacity of 16 million lb/hr.

Significance of Air Contaminant Emissions

The quality of air contaminant emissions in the manufacture of PCP is significant due to the fact that large numbers of compounds are emitted at high emission rates. The control of the emissions is desirable as a method of recovery of materials. Since PCP is toxic to human respiratory tracts and eyes, its very efficient control is recommended. The present control method which uses inadequate cloth area of bag filters needs augmentation.

Fumigant - Paradichlorobenzene

About 50 percent of the paradichlorobenzene (PDCB) is used as lavatory space deodorant, about 40 percent in moth control, and the rest as reactive intermediates in the production of chemicals suc. as agricultural pesticides and as an industrial porosity control agent.

PDCB causes moderate irritation to the human eye, throat, nose, and skin, with severe problems on long exposure. Continued exposure to PDCB vapors for months or years causes headache, portal cirrhosis, or atrophy of the liver.⁽¹⁾

PDCB undergoes biological, nonbiological, and sunlight degradation at a moderate to rapid rate.

Production Inventory

Paradichlorobenzene is manufactured by eight companies in nine states. These companies, their plant design capacities, and estimated 1974 production are given in Table 13.

The annual U.S. capacity is about 150 million pounds. Capacities are flexible and throughput depends on demand and available feedstocks. Benzene has been in very short supply recently due to decreased petroleum supplies. The production for p-dichlorobenzene in 1972 and 1973 was 77.3 and 85 million pounds, respectively, and the 1974 production is estimated to show a moderate increase of about 93.5 million pounds. Generally, production has varied from 50 to 60 percent of plant capacity.

Future Production Trends

Based on demand and raw material availability, production of PDCB is estimated to increase by about 2 percent per year through 1977.⁽¹¹⁾ Various arguments have been presented for growth projection. Some feel that the growth rate will be at least in line with gross national product and an increase in disposable income, while others feel that continued rise of polyester and newer synthetic fibre at the expense of wool and cotton would tend to level off production.

Two smaller suppliers of PDCB have withdrawn from the market since 1970, but expansions by others in the business have more than compensated. Most producers see little or no growth for p-dichlorobenzene. Still, there is strong feeling by some that the demand for the space deodorant used in restaurants, public buildings, etc., will continue to grow and the moth control market will hold its own.⁽¹¹⁾ Projections up to the year 1980 were provided in Table 1, and the production by the end of the decade is estimated at 112 million pounds.

Company	Location	Annual Capacity, lb x 10 ⁶	1974 Production 1b x 10 ⁶
Allied Chemical Corp., Industrial Chems. Div.	Syracuse (Solvay), N.Y.	12	9.0
Chemical Products Corp.	Cartersville, Ga.	3	NA
Dow Chemical Co.	Midland, Mich.	16	NA
Monsanto Industrial Chemical	Sauget, Ill.	12	NA
PPG Industries, Inc. Industrial Chem. Div,	Natrium, W. Va.	21	NA
Solvent Chemical Co., Inc.	Malden, Mass. Niagara Falls, N.Y.	5 (a) 10	12.0
Specialty Organics, Inc.	Irwindale, Calif.	2 ^(b)	2.0
Standard Chlorine Chemical Co., Inc.	Delaware City, Del.	60 ^(b)	24.0
	TOTAL	141	

TABLE 13. PRODUCERS OF PARADICHLOROBENZENE IN THE UNITED STATES (3,4)

(a) Production will be phased out in late 1974.

(b) These are processors--they buy crude mixed chlorinated benzenes and purify them.

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Manufacturing Process

Paradichlorobenzene is produced almost entirely as a by-product from the manufacture of monochlorobenzene, which is produced by the chlorination of benzene. Generally, prolonged chlorination is used to produce various by-products besides PDCB, as shown in the following reaction chemistry:



Benzene and chlorine are reacted in a chlorinator. The product is neutralized by sodium hydroxide with the recovery of dichlorobenzene. The production and waste material handling are shown in Figure 12.



FIGURE 12. PRODUCTION AND WASTE HANDLING SCHEMATIC FOR PARADICHLOROBENZENE⁽¹²⁾

Raw and Waste Material Handling

The essential raw materials used in the manufacture of PDCB are: bunzene, chlorine, and sodium hydroxide. The main toxic materials that need special handling during PDCB manufacture are chlorine, HCl, and PDCB. Most firms do edopt some precautionary measures for their employees such as wearing of plant coveralis, rubber gloves, goggles, safety glasses, hard hats, and face shields and respirators when necessary.

The material flow within a typical plant is shown in Table 12. At Dow Chemical, the HCl by-product is apparently recycled to chlorine production while trichlorobenzenes are recovered.

At Monsanto, the HCl is recovered as muriatic acid with only small amounts escaping through vents or going to a waste treatment plant. The PDCB work area is ventilated and the exhaust air goes to a wet scrubber. Monsanto is reported to monitor the PDCB concentration level.

Air Contaminant Emissions, Sources, and Rates

Sources of air emissions are chlorinator, PDCB recovery system, and the press room. The pollutants emitted are hydrochloric acid, chlorine, benzene, chloropenzene, and PDCB. Data are unavailable on the rates of emission of these compounds, making the nationwide emission status difficult to estimate. Pollutants emitted from various sources are presented in Table 14.

Minor emissions such as chlorine and HCl are given off at the wastewater treatment plant.

Air Contaminant Emission Control

Among the pollution control equipment used to control the gaseous and particulate emissions are wet scrubbers and absorption columns. An estimate of control efficiencies at the Standard Chlorine Company is presented in Table 15.

Sources of Emissions	Particulates	Rates; lb/hr	Ga	ses/Vapors	Rates, 1b/hr	Odor	Rates, Odor Units/hr
Manufacturing Processes							
Chlorinator			(1) (2) (3) (4)	HCl Benzene Chlorobenzene Cl ₂		Same Same Same	
P-dichlorobenzene Recovery	PDCB Chloride			Chlorobenzene		Same	
Press Room	PDCB					Same	
Wastewater Treatment							
			(1) (2)	C1 HCI		Same	

TABLE 14. AIR POLLUTION EMISSIONS, SOURCES. AND RATES FROM PARADICHLOROBENZENE MANUFACTURE AND WASTE TPEATMENT

.

Water Dovice	Efficiency,* percent		Comprund Controlled
Water Scrubber	90	(1)	нсі
		(2)	Benzene
		(3)	Chlorobenzene
		(4)	Dichlorobenzene
		(5)	Paradichlorobenzene
Absorption	95	(1)	HC1
Column		(2)	Chlorobenzene
		(3)	Benzene

TABLE 15. AIR POLLUTION CONTROL AT STANDARD CHLORINE

* Controlled emission data were not provided by any one company.

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some companies, for example, Allied, Solvent, and Specialty, with annual capacities around 10 million pounds, do not utilize control devices. They argue that it will be too restrictive if they are compelled to have all p-dichlorobenzene operating areas confined and exhaust air sent through a scrubbing system. The size of the control hood will be too large due to the extensive area involved.

Nowever, Standard Chlorine has controls in place (water scrubber and column absorber as given above) and the Monsanto Industries controls by means of water scrubber only. The press room is not controlled. Emission from this area is primarily PDCB.

The acceptable level of paradichlorobenzene used as the Threshold Limit Value by American Conference of Governmental Industrial Hygienists (ACGIH) is 75 ppm. It is not known whether the concentration in the press room exceeds this range, since there are no measured data.

Control Cost

Standard Chlorine provided the following control costs. Standard has an annual design capacity of 50 million pounds.

Control System	Size	Capital <u>Cost(\$)</u>	Operating <u>Cost(\$/yr)</u>
Water Scrubber(2)	48" & 16"	28,000	40,000
Carbon Absorption Columns		100,000	NA

Significance of Air Contaminant Emission

The nature of the pollutants emitted during the manufacture of PDCB requires that these substances be controlled. The control of PDCE to about 75 ppm in the working area is significantly important because of its high toxicity to humans.* There are no source emission standards for these compounds for the industry. Comparison with standards, if any, established for similar industries is not possible since the emission rates are not known. Further study is, therefore, required to be able to adequately assess the significance of these emissions.

* 75 ppm is the toxic level for humans.
SECTION V

REFERENCES

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APPENDIX A

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SUMMARY OF THE SELECTED PESTICIDES AND THEIR PRODUCERS



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APPENDIX B

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SUMMARY OF NONPROPRIETARY INFORMATION OBTAINED FROM THE SURVEY OF PESTICIDE PLANTS

Pesticide		Sources	Major Compound Emitted	Rates, 1b/hr
Methyl Parathion	ι.	Reactor	^Р 2 ⁰ 5 Н _а S	460
	2.	Chlorinator	"2" HCi	400
	- •		S	420
	3.	MPT Unit	NaC1	460
	4.	Waste Treatment Incinerator	so,	1550
			P205	
		Wastewater	H ₂ S	
			Mercaptan	
Toxaphene	1.	∂ -Pinene Production	N.A. ^(#)	
	2.	Camphene-Production	N.A.	
	3.	Chlorination - Toxaphene	HC1	
			C1,	4350
	4.	Toxaphene Granular Production	Toxaphene	
	5.	Wastewater Treatment	C1,	
			нсі	
MSMA	l.	Sodium Arsenite Production	As,0,	6.44 x 10 ⁻⁸
	2.	DMSA	CH ₂ C1	
			снуон	
			(CH3) 0	
	3.	MSMA Froduction	N ₂ SO ₄	
			MSMA	
	4.	MSMA Processing	MSMA	
	5.	Waste Treatment	N.A.	
Trifluralin	1.	Nitration	Salt of Nitrate,	· · · · · · · · · · · · · · · · · · ·
			sulfate, chloride	
			HF	1
			so ₂	3
			Nitrogen oxides	3
	2.	Condenser	CHC13	
			Trifluratin	

TABLE B-1. SUMMARY OF AIR CONTAMINANT EMISSIONS, SOURCES, AND RATES

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TABLE E-1.	SUMMARY	QF	AIR	CONTAMINANT	EMISSIONS,	SOURCES,	AND	RATES
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Pesticide		Sources	Major Compound Emitted	Rates, 1b/hr
Pentachlorophenol	1.	Pentachlorophenol	Chlorinated Phenol	
			сі ₂ нсі	
	2.	Acid System Seactors	Chlorinated Phenol	•
			HC1	
			C1,	
	3.	Ingot Casting	PCP	
	4.	Shotting Operation	PCP	
	5.	Wastewater Treatment	N.A.	
Paradichloro- benzene	1.	Chlorinator	HC1	
			Benzene	
			Chlorobensene	
			c1 ₂	
	2.	Recovery	PDCB	
			Chlorobenzene	
	3.	Press Room	PDCB	
	4.	Wastewater Treatment	с1 ₂ нс1	
			HC1	

(a) Not available.

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Pesticide	Source of Information	Control Device	Efficiency	Capital	Operating
Methyl Parathion	Monsarito	Incinerator (H ₂ S, S, mercaptan) ^(a)	(b)		
	Monsarito	Water Scrubber (P205, HCl)	9 5		
	Monsarto	Brink Mist Eliminator (P205 for visibility)	99 .9		
Toxaphene	Hercules	Alkali and Water Scrubber (solvent vapor, HCl, Cl ₂	,)		
	Hercules	Stripping (solvent vapor, HC1, C1 ₂)			
	Hercules	Limestone Adsorption (solvent vspor, HCi, Ci,)	100		
	Hercules	Baghouse (toxaphene)			
hsha	Diamond	Baghouse (As ₂ 03)		8,000	200
	Ansul	Water Scrubber (As ₂ 0 ₃)			
	Diamond	Acidifier Vent Scrubbers		500	100
Trifluralin	Eli Lilly	1- and 2-Stage Venturi Scrubber and Tri-mer Wet Scrubber	90	1,000,000	
Pentachlorophenol	Reichhold	Packed and Venturi Scrubber (Cl ₂ , Phenol, acids)	99-100	80,000	1,000
	Reichhold	Bay Filters (PCP)	95-99	70,000	6,000
	Reichhold	Mechanical Seals (for PCP reactor)		50,000	6,200
Paradichlorobenzene	Standard Chlorine	Water Scrubbers	90	28,000	40,000
	Standard Chlorine	(HCl, benzene, chlorobenzene, etc.)			
	Standard Chlorine	Absorption Column	95		
	Stendard Chlorine	(HCl, benzene, chlorobenzene)		100,000	

TABLE 8-2. SUMMARY OF AIR EMISSION CONTROL DEVICES, EFFICIENCY, AND COST

(a) Compounds in parentheses are controlled by the proceeding control device.

(b) Blanks show data not available.

TABLE B-3. LIST OF CONTACTS HAVING EXPERTISE AND SOURCES OF SIGNIFICANT INFORMATION ABOUT SELECTED PESTICIDE INDUSTRIES

Representative, Affiliation, Address and Telephone Number	Comment on Usefulness of Contact
The Ansul Company	Production data and control
Alan L. Haase	given.
Marinette, Wisconsin 54143	
(715) 735-7411	
Diamond Shamrock Chemical Company	Production data, control
W. R. Taylor	method, and costs given.
1100 Superior Avenve	
Cleveland, Ohio	
(216) 694-5000	
Hercules Incorporated	No production data, simple
H. E. Hicks	statement on process.
Brunswick, Georgia 31520	
Eli Lilly and Company	No production data.
Arlie J. Ullrich	Emission data given.
Indiarapolis, Indiana 46206	
Monsanto Industrial Chemicals Company	No production estimates,
P. E. Heisler	but control methods and
Sauget, 111inois 62201 (618) 271-5835	costs were provided.
Reichhold Chemicals, Inc.	Very good response.
J. C. Manlove	Estimates of production dat
P. O. Box 1482	production and control flow
Tacoma, Washington 98401	sheet and costs.
Standard Chlorine Chemical Company, Inc.	Production data, control
2. F. Romano	method, and cost given.
1035 Belleville Turnpike	
Kearny, New Jersey 07032	
(201) 997-1700	
Stauffer Chemical Company	Production data only,
Dan Simmons	
Mt. Pleasant, Tennessee	
(203) 226-1511	
Vulcan Materials Company	Production data, control
R. A. Bondurant, Jr.	method, and cost provided.
P. O. Box 545	-
Wichita, Kensas 67201	
(316) 524-4211	

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APPENDIX C

SAMPLE OF LETTER MAILED TO SELECTED PESTICIDE MANUFACTURING COMPANIES

August , 1974

Gentlemen:

Battelle's Columbus Laboratories under contract to the Strategic Studies Unit of the Office of Pesticide Programs, Environmental Protection Agency is working to develop background information and determine the significance of emissions from pesticide plants.

For this study, the following six pesticides have been selected:

- (1) Insecticides Methyl Parathion and Toxaphene
- (2) Herbicides MSMA and Trifluralin
- (3) Fungicides and Wood Preservative Pentachlorophenol
- (4) Fumigant P-Dichlorobenzene.

One of the objectives of this information gathering is to obtain factual information from the manufacturing industries so that determination can be made of

- (1) The extent of ambient emission of the pesticides
- (2) The type of compounds emicted
- (3) Currently employed mechods of emission control.

From the above data, the study will seek to project future emissions, relate it to similar emission from other sources, and thus obtain a quantitative estimate for the significance of pesticide emissions from the manufacturing sector.

Please find attached a list of six questions, which we request you to complete and return to us at your earliest convenience. We will keep any information you supply within BCL files so that the confidentality of your data is preserved.

We appreciate your willingness to cooperate and would like to assure you that any assistance you will provide will be of immense value to this study required under the Clean Air Act of 1970.

Cordially,

C. N. Ifeadi Research Scientist Waste Control and Process Technology Section

Attachment: Questionnaire

71.

Name of Manufacturing Company _____

Address

Name, position, and phone number of person responding

Name of posticide produced _____

<u>Question 1</u>. Design Capacity and Production

Ycar	Design Capacity, millions of lb	Months In Operation	Actual Production, <u>millions of lb</u>
1970			
1971			······································
1972	and the second	······	
1973	<u> </u>		
1974 (Estimate)			
1975 (Estimate)			

Provide details of any the nicel or economic situation that may affect future increases or decreases in your plant production.

Question 2. Process Description

Give a briaf description of the processes used to produce the pesticide. Specify the raw materials, by-products, and waste materials. Amplify with <u>simple</u> production chemistry and attach simple flow sheets.

Question 3. Raw and Waste Material Handling with the Plant

Particular attention is generally paid to materials handling within the plant, since the raw and waste materials may have high toxicity. Briefly descrube the precautions taken in your plant.

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	Emission Sources	Compounds Emitted	Controlled Yes or No	Method of Control	Emissions (1b/ton)*	Efficiency (%)
<u>Manufacturing Plant</u> <u>Site</u>						
Particulates						
Gases						
Odor						
Waste Disposal Site						
Farticulates						
Gases						
Odor						

Question 4. Air Contaminant Emissions and Control

* Or any other unit employed by your facility.

Describe briefly the emission control system used in your plant for particulates, gases, odor, and visibility control. Describe problems of visibility and odor, if any, around your plant. Information or nature of odor complaints, if any, from the public in your area will be useful in obtaining an idea of the odor problems associated with your plant. Question 5. Cost of Emission Control System

Name of Control System	Size	<u>Capital Cost (\$)</u>	<u>Operating Cost (\$/yr)</u>
and This is a second		ي پي مينيا که اور اين و ماندان و ميرون و ماندان و . رو و ماندان اين و ماندان و مان	الم میں بین کار میں الکر میں الم اور اللہ والف الی والی کار میں اللہ میں اللہ والی والی کار میں اللہ والی میں ا

Question 6.

Please indicate the status of air emissions from your facility as (a) acceptable (b) needs improvements? Comment on the economic impact of restricting the emissions from your plant to levels considered (a) reasonable (b) too restrictive. State what you think these levels should be.