ASSESSMENT OF POTENTIAL SOURCES OF RELEASE OF DIOXIN TO THE ENVIRONMENT FROM REPORTED MANUFACTURING OPERATIONS AND ACTIVITIES AT THE DIAMOND SHAMROCK FACILITY

80 LISTER AVENUE
NEWARK, NEW JERSEY

PREPARED FOR

DEFENSE STEERING COMMITTEE

(DIAMOND SHAMROCK V. AETNA, ET AL)

MAY 29, 1987

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819-001-04

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Attention: Stephen D. Cuyler, Esq.

Re: Report
Diamond Shamrock v. Aetna, et al

Gentlemen:

This report presents the results of our review of information regarding operations and activities at the former Diamond Shamrock facility at 80 Lister Avenue, Newark, New Jersey, for the purpose of assessing potential points of release of dioxin (2,3,7,8-TCDD)-containing material from this facility into the environment. This assessment is based on a review of certain documents contained in the Discovery Documents File and depositions of former Diamond Shamrock employees involved in 80 Lister Avenue plant operations made available to PS&S by the Defense Steering Committee.

Very truly yours,

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ASSESSMENT OF POTENTIAL SOURCES
OF
RELEASE OF DIOXIN TO THE ENVIRONMENT
FROM REPORTED
MANUFACTURING OPERATIONS AND ACTIVITIES
AT THE
DIAMOND SHAMROCK FACILITY
80 LISTER AVENUE
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1.0

SUMMARY

1.0 SUMMARY

Information regarding operations and activities at the former Diamond Shamrock facility at 80 Lister Avenue, Newark, New Jersey, was reviewed for the purpose of assessing potential points of release of dioxin (2,3,7,8-tetrachlorodibenzo-p-dioxin) -containing material from process operations into the environment. This information consisted of depositions of former Diamond Shamrock personnel and certain discovery documents provided to PS&S by the Defense Steering Committee and other pertinent references. This assessment has targeted several points in the 2,4,5-trichlorophenol (TCP) and 2,4,5-trichlorophenoxyacetic acid (T) manufacturing process as potential points of discharge. Many of these points relate to incidental releases, such as leaks and overflows in the processing equipment. In addition, release of dioxin-containing materials apparently resulted from conscious waste management and maintenance procedures, such as wastewater discharge and equipment cleaning.

Airborne emissions (particulates, fumes) were likely a source of dioxin migration. The available information indicates that, during the 1950's, emissions from the TCP building were discharged to the atmosphere by exhaust fans. The documents reviewed also indicate that fume exposure was present in TCP production, and that chloracne problems were troublesome around the autoclave. According to John Burton, the plant manager in the 1950's, the pressure from the autoclave was relieved by venting to the atmosphere after each autoclave batch reaction, indicating gaseous and likely vapor releases to the atmosphere. Based on Diamond Shamrock operating reports from the period November 1966 to July 1969, about 58 autoclave batch reactions occurred per month.

The venting system reportedly posed "problems of contamination" as noted in a November 1968 operating report. The TCP intermediate storage tank and the anisole still were also noted as points for which "remedial work" was reportedly undertaken.

Reportedly, organic particulates were controlled to 10 pounds per day by a scrubber by the late 1960's, with sodium trichlorophenate (NaTCP) "mist" emissions controlled to 0.06 pounds per hour from the 1.2 pounds per hour that would have been emitted on an uncontrolled system. Scrubber effluents in which dioxin was likely present would have been discharged to the sewer, to a pit near the river, or to the river. Sources to the scrubber included losses from the T reactor, vapor losses from acidification and dust formed in the flaking process.

The 1960 explosion in the autoclave where NaTCP was being manufactured could have released as much as one-third of a pound of dioxin. The explosion may also have indirectly caused dioxin discharge by disturbing "concrete slabs" and "drums" in the area. Other incidental discharges may have resulted from at least five rupture disc releases, aside from the 1960 explosion, causing releases of material to the atmosphere, to the river, and possibly to a pit.

Discharges also occurred from reported leaks in the autoclave, from the TCP recovery tank which "burped over" on at least one occasion, from reported leakage in the acidification tank, and possibly from the TCP intermediate storage tank which reportedly presented a "pollution and safety hazard." According to a 1968 operating report, TCP was also lost due to its limited solubility in acid-water and, when wastewaters were discharged, the solubilized TCP possibly carried some dioxin with it. In addition, NaTCP storage tank residue flushing would have likely caused the release of dioxin-containing materials into the environment.

Also suspected for their potential to release dioxin are the stripping unit, which separated anisole from NaTCP, and filter units, which separated product streams from impurities. According to former Diamond Shamrock employees, the stripper residues were flushed into the river or to a sewer sump, while a small amount of spillage occurred at the unit's sample tap. The condenser tubes in the unit also had leakage problems, while process wastewaters from the stripper were routed to the river. With respect to filters, dioxin would likely have accumulated in filter cakes. Dioxin also was likely carried over into product or with filter washwaters, which, in turn, were sometimes discarded. In addition, the sewering of acid used to regenerate the carbon purification column was another means for the release of dioxin into the environment.

The T area was also a likely source of release of dioxin-containing materials. The T centrifuge and a manhole on the T reactor were reportedly sources of fume exposure, while odor problems and evidence of material discharge reportedly existed during the process of flaking T acid. Particulate releases from this flaking operation were a likely source of release of dioxin-containing materials.

Plugging problems in lines and pumps were reported in depositions and operating reports. Disassembling and flushing of pipes, as well as reported leakage in transfer and product lines, would have contributed to further releases of dioxin. Leaks occurred in the reslurry tank, and molten acid was observed "going overhead" in a "Luwa" dryer. T pumps experienced discharges because of the abrasive nature of the product being transported. Maintenance problems were also reported in the ester area. Besides maintenance and process difficulties, process washwater discharges again were a likely source of release of dioxin-containing materials.

Process wastewaters were discharged in large volumes to the Passaic River before 1956. These discharges continued after 1956 with some of the wastewaters going to the sewer. Reportedly, 100 tons of unrecycled 2,4,5-T effluents per year were discharged into the Passaic River in 1959. Sources of these wastes include filter and ester washwater.

Sewer and sump samples reported in a 1985 report prepared for Diamond Shamrock by I.T. Corp., et al, titled "Site Evaluation, 80 Lister Avenue" noted eight sumps that were sampled. All samples contained dioxin ranging from 19.5 to 9160 parts per billion (ppb). Materials that were discharged to the sumps reportedly included discharges from the TCP area, sulfuric acid from the scrubbers, process streams related to the anisole stripper, and chlorophenolic wastes. Process wastewaters were routed to a sump in the area of the manufacturing building (2,4-dichlorophenoxyacetic acid (D) and T), with the overflow discharging to a sewer. Cleaning of accumulated residues from the sumps was reportedly a "dirty, messy operation" which might have resulted in the discharge of dioxin-containing materials.

According to depositions, there are indications that general maintenance and housekeeping practices also contributed to dioxin releases. Maintenance would have included flushing of residue from process vessels and discarding of old pipes and debris. "Gunk from tanks" was reportedly discarded during plant shutdown. Some evidence of "poor housekeeping" was also noted at the riverfront, where drums and equipment were reportedly stored on a concrete pad. In addition, spillage in quality control sampling procedures and disposal of unused or wasted samples would have resulted in further discharge of dioxin into the environment.

Packaging and transport would likely have contributed to some release of dioxin-containing materials. The "bagging" area reportedly had a certain amount of dust, and any spillage in loading and transport for shipping may have gone into the ground since depositions did not indicate any special practices of isolating or cleaning up spills. Furthermore, truck traffic likely provided an additional means for dioxin-contaminated dust migration in the vicinity of the site.

The aforementioned 1985 report projected that 96.2 pounds of dioxin are contained in the soil at the 80 Lister Avenue site. Based on an assessment of potential dioxin (2,3,7,8-TCDD) content in documented releases, the total projected amount of dioxin would appear to be far less than the 96.2 pounds reported. This assessment suggests that the bulk of the dioxin on site arose from routine process emissions through leaks and operations that allowed for material to be lost. Based on available discovery documents, such as depositions and operating reports from the late 1960's, it appears that these discharges were likely persistent throughout the period of operation of the Diamond Shamrock plant.

2.0

INTRODUCTION

2.0 INTRODUCTION

The information contained herein is a preliminary assessment of potential sources of release of dioxin-containing material from process operations at the former Diamond Shamrock plant at 80 Lister Avenue, Newark, New Jersey, during the period of its operation from 1951 to 1969. This assessment is based on a review of documents made available to PS&S by the Defense Steering Committee and on other available pertinent reports obtained by PS&S. Included in these documents are the following depositions in the matter of Diamond Shamrock Chemical Company, Plaintiff vs. The Aetna Casualty and Surety Company, et al., Defendants:

- Eugene Bak, April 8, 1987 (Diamond Shamrock 80 Lister Avenue process engineer, technical superintendent and production superintendent, 1961 to 1969)
- John Burton, March 18, 1987 and April 3, 1987, (80 Lister Avenue plant manager 1949 to 1960)
- Robert L. Chonoles, January 13, 1987 (Diamond Shamrock plant manager, 80 Lister Avenue facility, 1968 to 1969)
- Raymond A. Guidi, February 19, 1987 and February 20, 1987, (Diamond Shamrock acting plant manager and plant manager, 80 Lister Avenue facility, 1960 to 1963)
- Martin C. Heisele, March 5, 1987 (Diamond Shamrock 80 Lister Avenue process development chemist or engineer, 1958 to late 1962 or early 1963)
- Francis R. Kennedy, January 22, 1987 (Diamond Shamrock plant manager, 80 Lister Avenue facility, 1963 to 1968)
- James J. Lukes, February 17, 1987 (Diamond Shamrock employee 1948 to 1979; positions included manager of Research, Engineering and Customer Technical Services)
- Homer Smith, April 16, 1987 (Diamond Shamrock 80 Lister Avenue plant engineer (maintenance and utilities), 1952-1969.
- F. Gordon Steward, March 9, 1987 (Diamond Shamrock process engineer and technical superintendent, 80 Lister Avenue facility, 1965-1969)

Some of the other documents reviewed include:

- "Site Evaluation, 80 Lister Avenue," submitted to New Jersey Department of Environmental Protection, prepared by Diamond

Shamrock Chemicals Company, IT Corporation, Woodward Clyde Consultants, Enviro-Measure, Inc., Volume 1, dated February 1985.

- "Feasibility Study, 80 Lister Avenue," submitted to New Jersey Department of Environmental Protection, prepared by IT Corporation for Diamond Shamrock Chemicals Company, Copy No. 1, dated October 1985.
- "Site Evaluation Addendum 80 and 120 Lister Avenue," prepared by IT Corporation for Diamond Shamrock Chemicals Company, dated February 1986.
- "Report Prepared by Review of Documents Received From Diamond Shamrock Company, New Jersey," Fingerhut, Marilyn and Marlow, David, April 1, 1983.
- "Report on Lister Avenue Facility, June 10, 1983," Worthington, James B., Director of Environmental Affairs, Diamond Shamrock Corporation to Michael Catania, Office of Regulatory Services, Department of Environmental Protection.

Depositions and other documents will be reviewed by PS&S as they are made available by the Defense Steering Committee.

Also available for review are aerial photographs of an area which includes the 80 Lister Avenue site taken in the period 1940 to 1974. The date of each photograph is as follows:

- April 6, 1940
- April 7, 1951
- April 23, 1961
- April 7, 1969
- April 11, 1974

Following the report Summary and the General Process Description of the production of 2,4,5-trichlorophenol (TCP) and 2,4,5-trichlorophenoxyacetic acid (T), several specific areas of potential discharge of dioxin-containing materials are addressed in subsections 4.1 to 4.12. In each of these subsections, a brief list of pertinent potential sources of discharge is followed by a discussion of the particular subsection. Referenced items are included in Appendix A: References.

Section 5.0 addresses specifically the possible amounts of dioxin which may have been released as a result of given plant operations at the 80 Lister Avenue, Newark Diamond Shamrock plant. This analysis is based on information discussed in Section 4.0.

3.0

GENERAL PROCESS DESCRIPTION

3.0 GENERAL PROCESS DESCRIPTION

The following brief description of the TCP and T processes is based primarily on information contained in James B. Worthington's report as Diamond Shamrock's Director of Environmental Affairs to the NJDEP [1] and in Marilyn Fingerhut and David Marlow's report based on a review of documents sent to NIOSH by Diamond Shamrock [2]. Other sources used are referenced appropriately. This summary is intended to serve as an overview of the major aspects of the process.

Figure 1 is a sodium trichlorophenate (NaTCP) process flow diagram as represented from the Fingerhut and Marlow report. Figure 1 depicts the process as it existed in the 1960's. In this process, methanol is pumped to a methanol/caustic mix tank. Some of this methanol is fresh and some is recycled from later in the process. Flake caustic is added from 50-gallon drums, and the caustic (NaOH) and methanol (CH_3OH) react to form sodium methylate (CH_3ONa) and water (H_2O).

The tetrachlorobenzene is pumped from steel tanks to a drop tank at 165° C and is fed to one of two 1000-gallon jacketed stainless steel autoclaves [2a]. The sodium methylate is then added in a gradual controlled manner with constant agitation. This gradual method of addition of reactants differs from the charging of the autoclave in the period of operation before the 1960 explosion, where flake caustic, methanol, and tetrachlorobenzene were all added directly to the autoclave [2b].

The autoclave temperature is subsequently maintained at 165 to 175°C at a pressure of 370-375 pounds per square inch gauge (psig). Autoclave temperature is controlled by the use of steam and cooling water circulation through the jacket. The autoclave reaction, which is exothermic (gives off heat) and involves an intermediate reaction, is represented in Figure 1A.

NaTCP PROCESS FLOW DIAGRAM

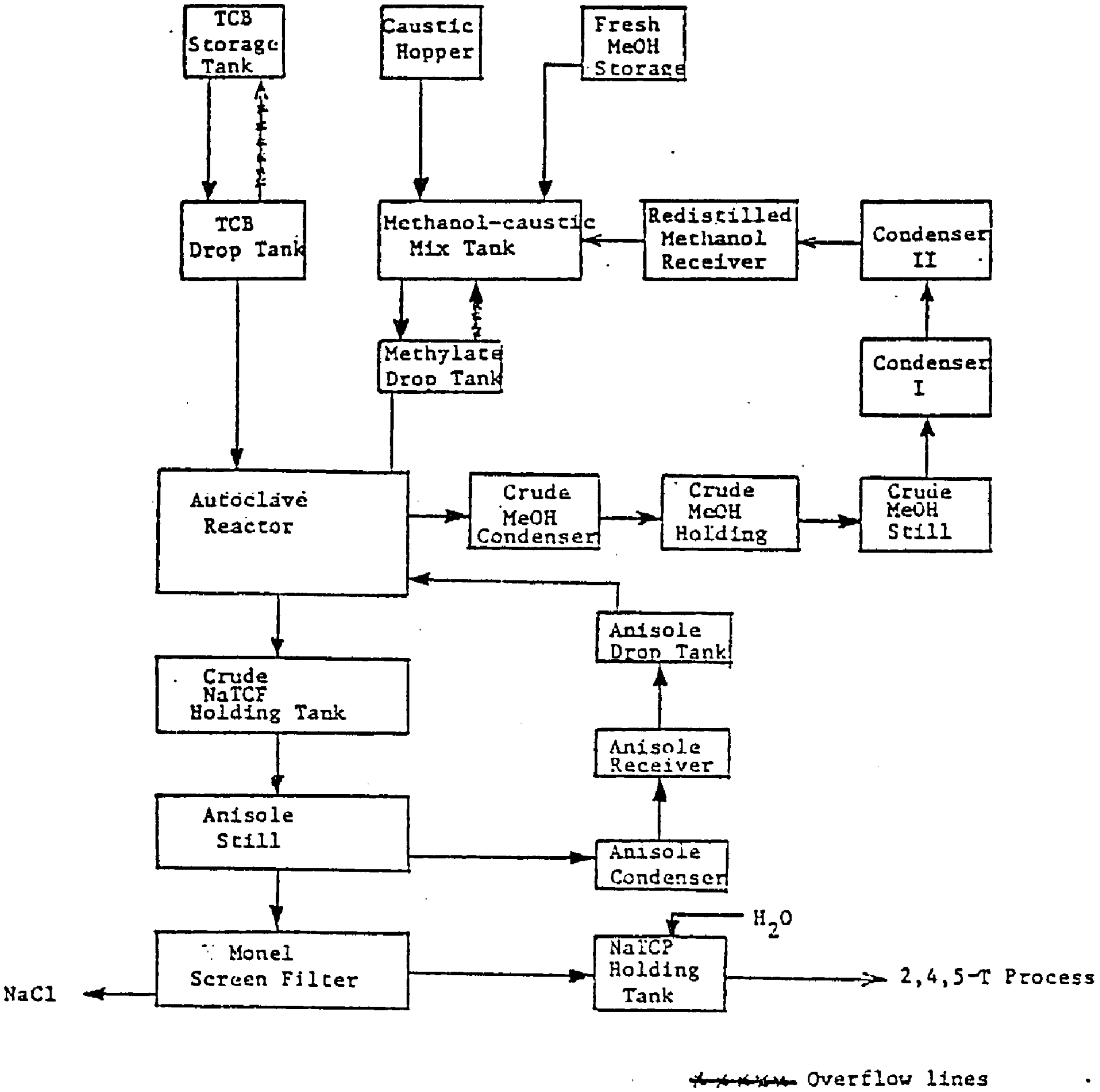

FIGURE 1

SOURCE: REFERENCE 2

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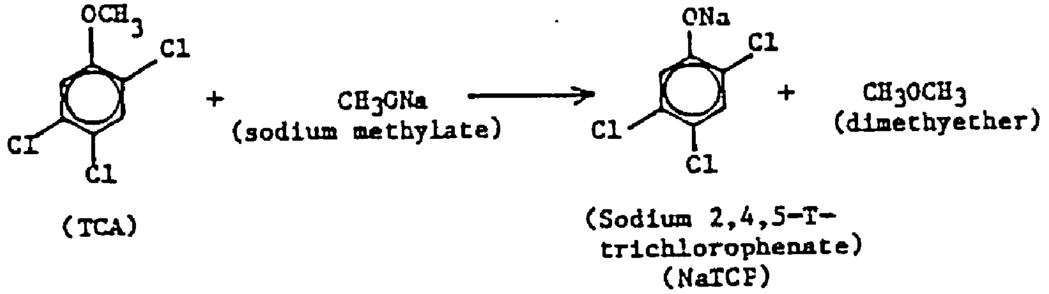
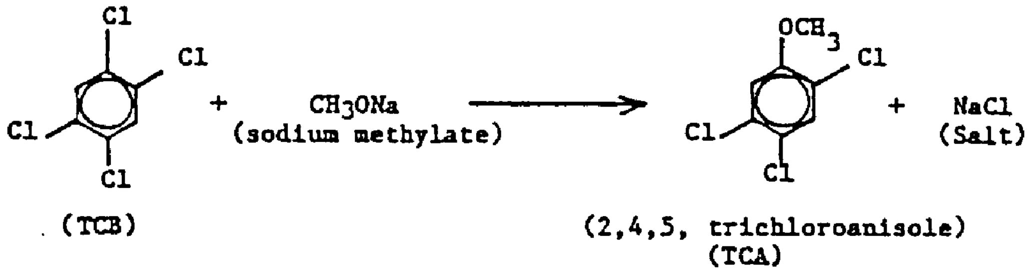
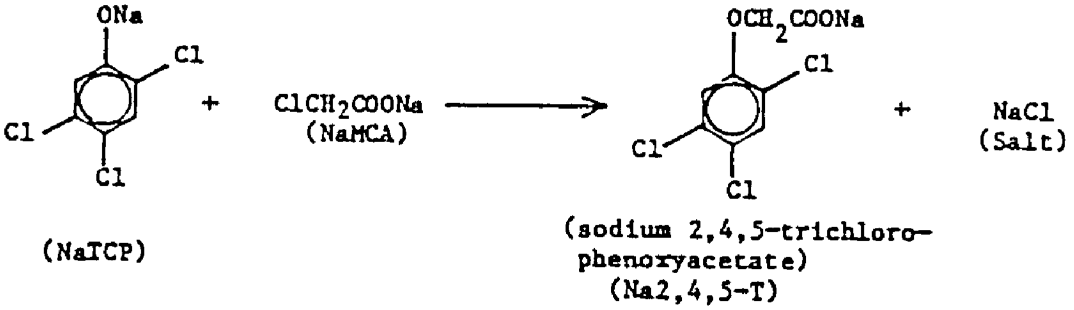


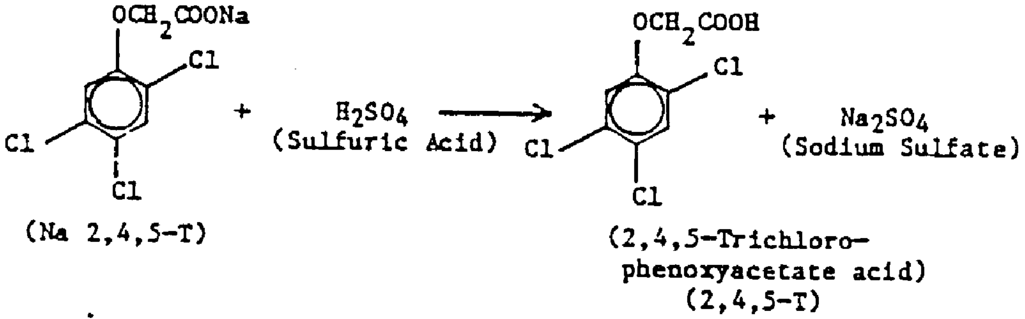
AUTOCLAVE FINAL REACTION



AUTOCLAVE INTERMEDIATE REACTION



Na-2,4,5-T REACTION



2,4,5-T ACIDIFICATION REACTION

2,4,5-TCP AND 2,4,5-T PROCESS REACTIONS

FIGURE 1A

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SOURCE: REFERENCE 2

The digestion period for the reaction is then 3 to 5 hours, and the reactor is then allowed to cool to 50-60°C. Dimethyl ether (CH_3OCH_3) produced in the reaction is released to the atmosphere through vents.

The next step is the raising of the autoclave temperature to 120°C to remove the methanol. The crude methanol is condensed and pumped to a crude methanol storage tank. It is then redistilled and pumped to a redistilled methanol receiver, where it is ready for recycling in future autoclave batches. The crude NaTCP is stored in the NaTCP hoding tank until six batches are completed.

The contents of the crude NaTCP holding tank are then pumped to the trichloroanisole (anisole) still. Anisole, an autoclave reaction intermediate and by-product (see Figure 1A for chemistry), is removed in this still by steam stripping the NaTCP. This means that steam is introduced into the stripping vessel, effecting the removal of water and impurities from the NaTCP in the form of a vapor. The anisole is recovered in the "overhead product" (condensed vapors) and is separated from the water, which is discharged to the sewer. When enough anisole is collected, it is substituted for tetrachlorobenzene in a batch.

The steam-stripped NaTCP now passes through a filter to remove sodium chloride and is subsequently (after 1967) purified in a carbon tower. The Fingerhut and Marlow report notes that the NaTCP is then pumped to a holding tank where it is diluted from a 36% NaTCP solution to a 25% NaTCP solution for use in T production or it is acidified to form TCP.

Figures 2 and 3 are flowsheets of the NaTCP process as represented in the Worthington report for the periods 1960-1969 and 1954-1960, respectively. The major differences in the processes as outlined by these figures is that the process in the period 1954-1960 did not have a methanol redistillation step or a filter after anisole stripping.

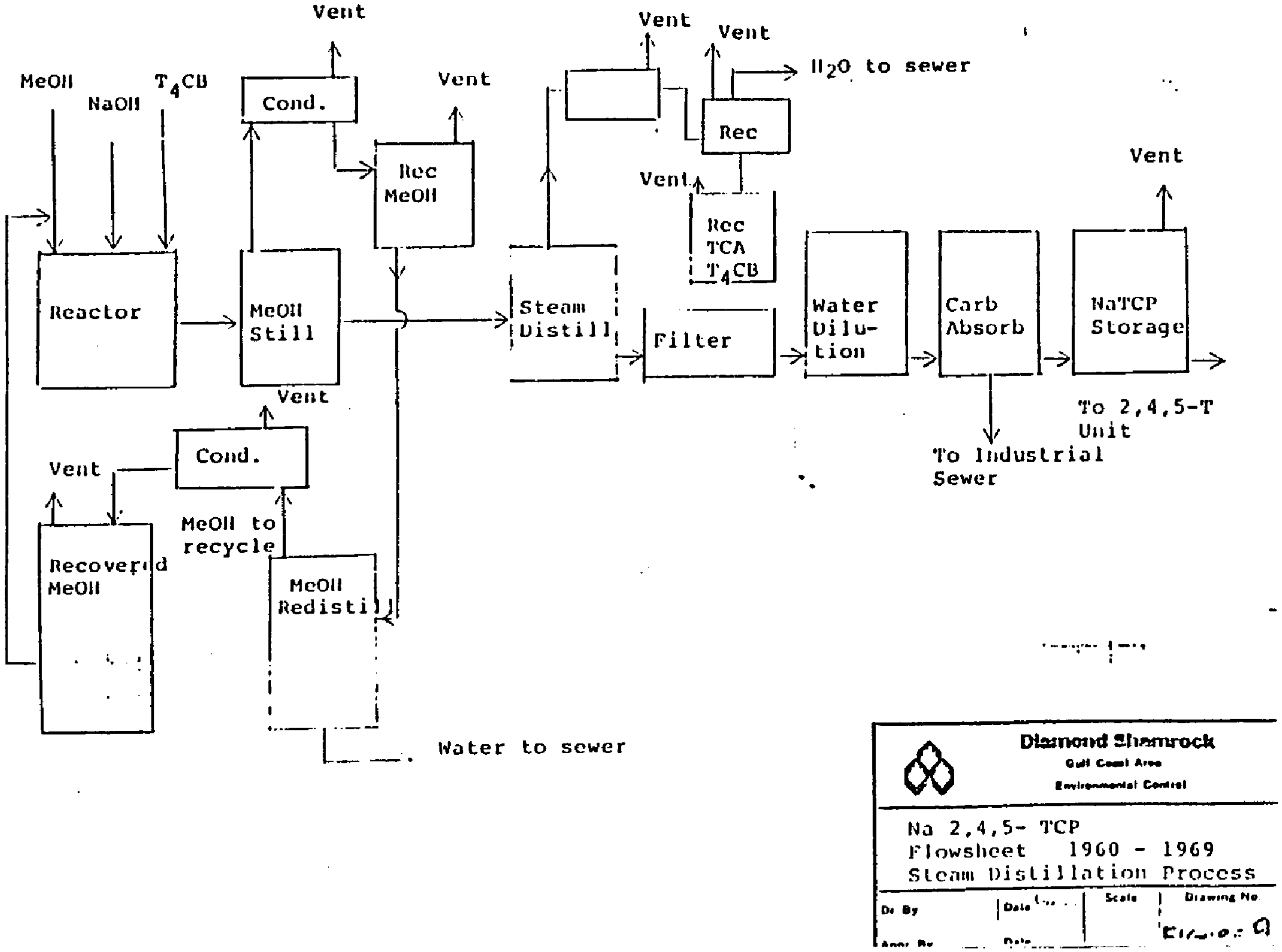

FIGURE 2

SOURCE: REFERENCE 1

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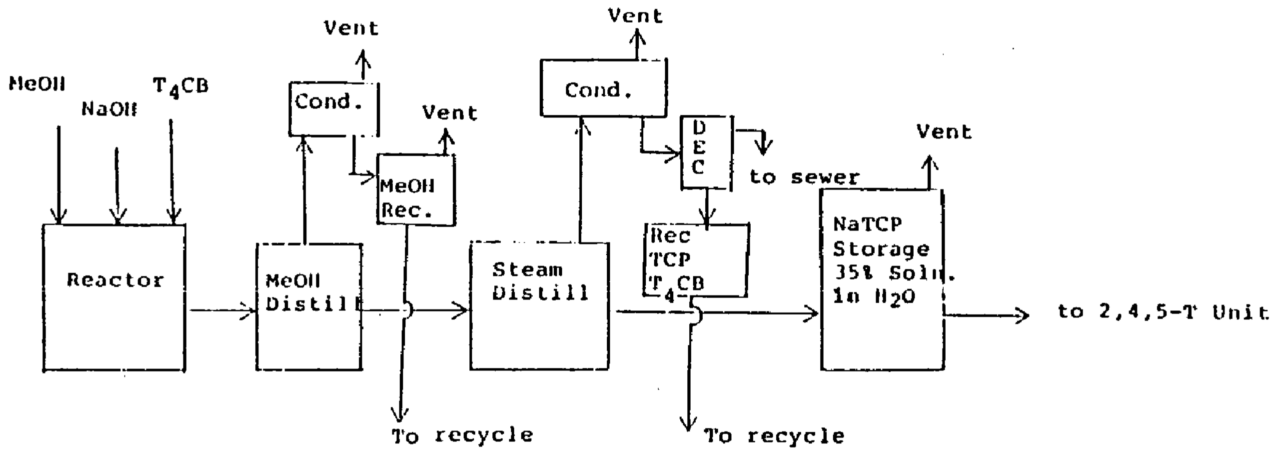

Diamond Shamrock

Environmental Control

Na 2,4,5-TCP
Flowsheet 1954 - 1960
Steam Distillation Process

Dr By	Date [illegible]	Scale	Drawing No
Appr By	Date		Figure 6

FIGURE 3

SOURCE: REFERENCE 1

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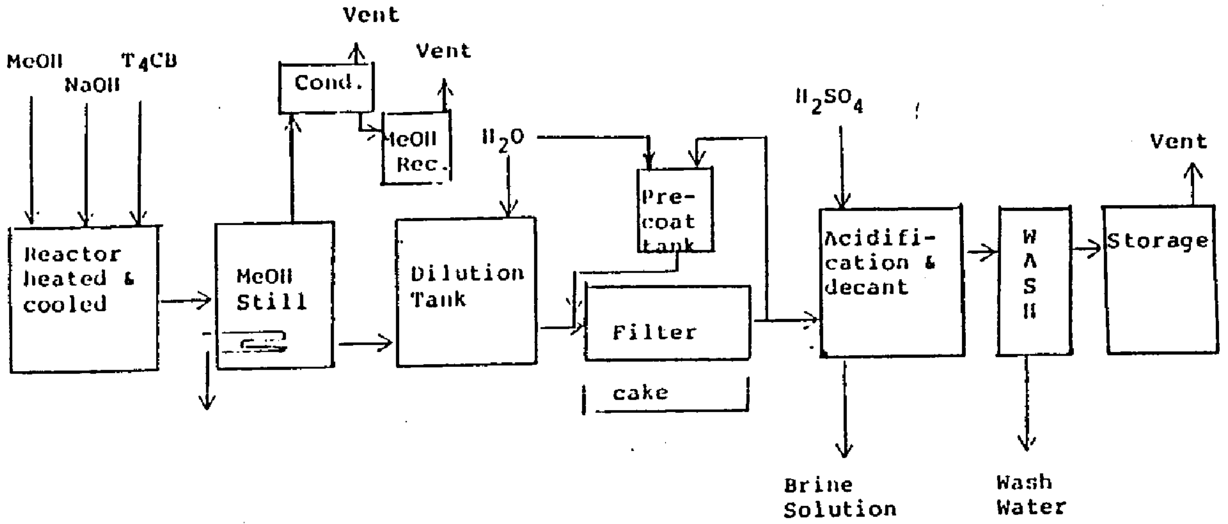
The NaTCP process from 1951 to 1954 as represented in Worthington's report is shown in Figure 4. In this scheme, the impurities in the NaTCP stream are not separated by a stripping column, but are removed by a dilution/filtration method. This method involved the dilution of the NaTCP solution to effect the precipitation of organic impurities and a subsequent filtration to collect these impurities in a filter cake. The solution is then acidified and decanted to recover the TCP, followed by washing and storage.

The next sequence of steps are related to the production of 2,4,5-T acid. This process flow diagram is shown in Figure 5 from the Fingerhut and Marlow report and the chemistry of the reaction is shown in Figure 1A. In this process step, NaTCP is charged to the reactor from a drop tank. Cooling water circulation through the reactor jacket and agitation are then commenced. Sulfuric acid and monochloroacetic acid are added. The reactor should now be at 70 to 80°C. The addition of a second charge of NaTCP from the drop tank is followed by the addition of caustic. The batch is then cooked at 95-100°C for about two and a half hours.

After the condenser reaction step, the Na 2,4,5-T is processed in a filter holding tank and a subsequent filter. Water soluble impurities and unreacted Na-2,4,5-TCP are removed using sodium sulfate spray washes. Na-2,4,5-TCP is recovered [2c,22] in a recovery acidification process. The Na 2,4,5-T is then pumped to a slurry tank and then to a primary acidification tank.

The acidification process is accomplished in a primary and a secondary acidification tank. This reaction (see Figure 1A) yields 2,4,5-T acid and sodium sulfate. The following steps then involve either a "hot-melt" process (1967 to plant shutdown) or a centrifuging operation (before 1967) [2d].

In the hot-melt process, the resulting molten mixture of 2,4,5-T



Diamond Shamrock
Environmental Control

Na 2,4,5- TCP
Flowsheet 1951 - 1954
Dilution Process

Dr By	Date 4/11/75	Scale	Drawing No. 5

FIGURE 4

SOURCE: REFERENCE 1

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FIGURE 3

2,4,5-T Process Flow Diagram

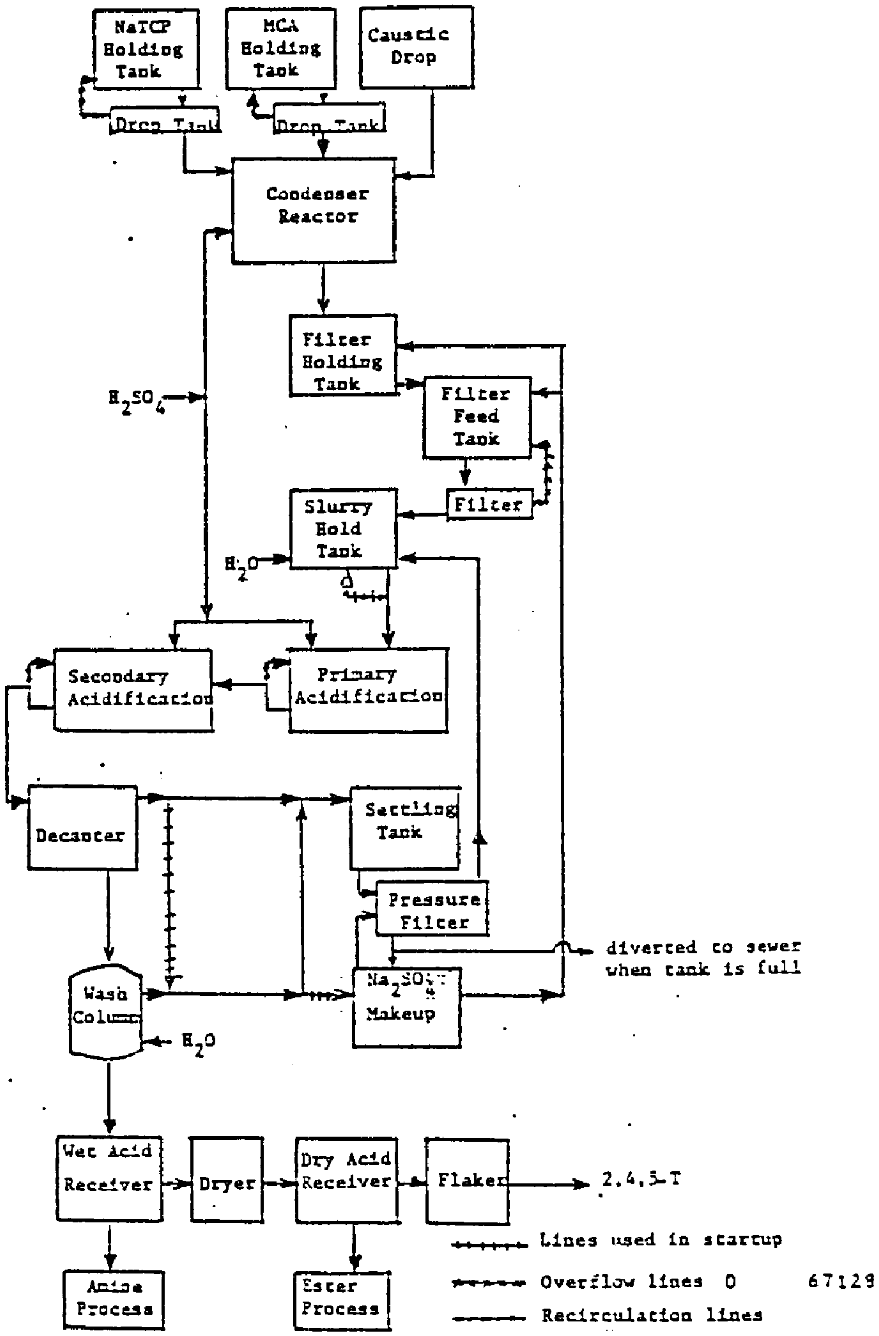

FIGURE 5

SOURCE: REFERENCE 2

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and impurities settles into an upper aqueous layer and a heavier (lower) 2,4,5-T layer in a decanter. The 2,4,5-T is then pumped from the bottom of the decanter while the aqueous layer overflows to a settling tank. The 2,4,5-T is then routed to a wash column, where it is washed with a countercurrent flow of hot water. The washed 2,4,5-T, which enters the column at the top and exits at the bottom no longer containing sodium sulfate, is collected in the wet acid receiver. From there, it is pumped to the dryer or to the amine process, where it is mixed with triethylamine.

The drying operation involves a dryer operating at 155-160°C and subsequent maintenance of 160-165°C in the dry acid receiver. The dried molten 2,4,5-T, after collection in the dry acid receiver, is either pumped to the flaker system to be bagged or is routed to the esterification unit. Esters produced included ethylhexyl and butyl-T esters.

In the pre-1967 process, the 2,4,5-T acid and sodium sulphate were centrifuged. The resulting moist but relatively free-flowing cake of 2,4,5-T was "plowed" from the centrifuge and discharged into dollies and/or carts [2e].

Na 2,4,5-T is recovered, in a settling tank, from the overflow of the decanter and wash column and in the hot-melt process as described by Fingerhut and Marlow. Cooling of the overflow results in the precipitation of Na 2,4,5-T solids, which are recovered in a pressure filter. Solids are periodically flushed back to the slurry tank for use in future 2,4,5-T batches, while sodium sulfate is recovered from the liquid in a sodium sulfate makeup tank by the addition of caustic soda for use as a spray wash in the first Na 2,4,5-T filter.

The route for formation of dioxin in the 2,4,5-TCP process is outlined in the EPA publication "Dioxins" (Esposito et al., November 1980) as follows:

> "Treatment of 1,2,4,5-tetrachlorobenzene with caustic yields 2,4,5-trichlorophenol. The reaction conditions are sufficiently drastic, including alkalinity and elevated temperature, to cause formation of the alpha-ketocarbene, which reacts with the chlorophenylate to give the predioxin, which then reacts to yield 2,3,7,8-TCDD."

Figure 6 is a chemical representation of 2,3,7,8-TCDD formation as depicted in "Dioxins." The EPA report seems to indicate that dioxins would be formed in the autoclave in the TCP process, where the above-noted reaction occurs. The report states that additional dioxins are probably not formed during 2,4,5-T manufacture, as the process temperature (less than 140°) is lower than the temperature needed to create dioxins. The "Dioxins" report, however, does not take into account the hot-melt drying temperatures of up to 165°C. "Dioxins" notes that a 1978 EPA report on 2,4,5-TCP production describes the present-day process as occurring at 180°C.

Except for the new materials introduced to the process, which included methanol, caustic, tetrachlorobenzene, acid, water and possibly other fresh streams, the process streams were capable of containing at least trace amounts of 2,3,7,8-TCDD.

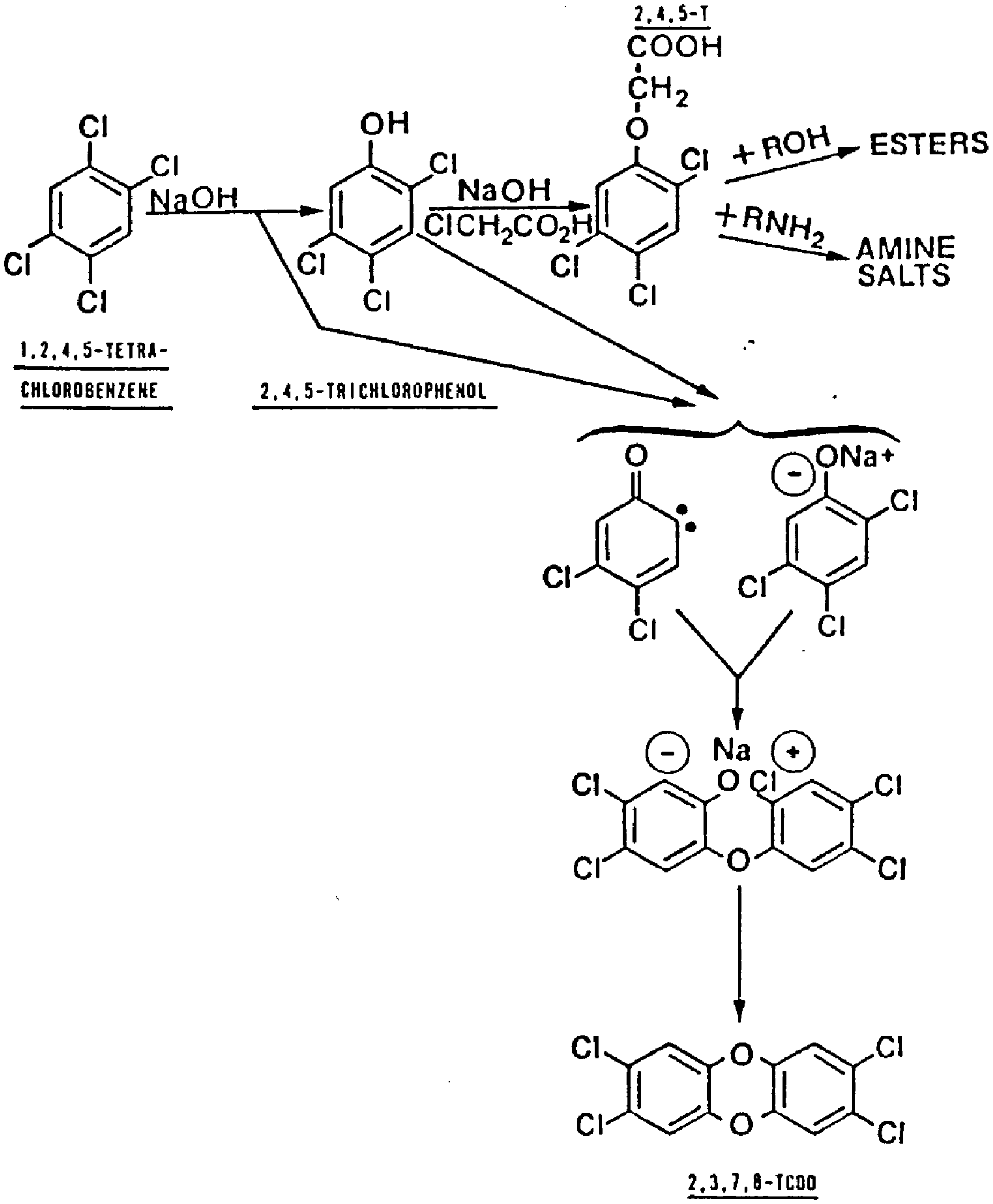

Figure 13. 2,4,5-Trichlorophenol, 2,4,5-T and esters and salts.

FIGURE 6

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SOURCE: EPA "DIOXINS"

4.0

POTENTIAL SOURCES OF DISCHARGES

4.0 POTENTIAL SOURCES OF DISCHARGES

The available documents reviewed during compilation of the information presented herein, as referenced in Section 2.0 of this report, appear to indicate that discharges of materials may have occurred in the following areas or process operations:

- 2,4,5-Trichlorophenol (TCP) Process
- 2,4,5-Trichlorophenoxyacetic Acid (T) Area
- Piping
- Pumps
- Distillation
- Filters/Centrifuges/Purification
- Vents/Scrubbers/Air Emissions
- Wastewater
- Sewers/Sumps
- Sampling/Quality Control
- Packaging/Transport
- Maintenance

With the exception of new streams which had not been exposed to the TCP or T streams during or after autoclave processing, all process streams are capable of containing at least trace amounts of dioxin.

4.1 2,4,5-TRICHLOROPHENOL (TCP) PROCESS

Discharges from the TCP process operations most likely occurred as follows:

- Fumes from TCP production;
- An autoclave explosion in 1960;
- Rupture disc releases;
- A "burp-over" in the TCP recovery tank;
- TCP lost in wastewater due to solubility in acid-water;
- Acidification tank leakage;
- Autoclave leakage;
- Autoclave flushing;
- NaTCP storage tank cleaning;
- Piping repair and flushing.

4.1.1 Chloracne

Chloracne is a skin disorder that has been associated with dermal exposure in the workplace to a group of chlorinated compounds, which includes dioxin (2,3,7,8-TCDD). Reports of chloracne problems among workers at the Diamond Shamrock facility are likely indications of dioxin releases since they suggest that operations personnel were able to come into direct contact with dioxin-containing materials.

According to depositions of Burton and Steward, chloracne problems were most troublesome around the autoclave [3] as TCP operators seemed to be among the first to get chloracne [4]. There was reportedly some fume exposure related to TCP production [5a]. Burton noted that ventilation and housekeeping in the TCP building were not "up to par." Examples given by Burton of the building not being "up to par" for chemical manufacturing were "in connection with the ventilation, in connection with housekeeping, in connection with isolating one unit, such as normally a trichlorophenol unit should be isolated by itself" [5b].

Chloracne at the Diamond Shamrock facility was evidenced at least as far back as 1955, after the 1954 introduction of steam stripping [6,7]. This May 1955 chloracne outbreak may also have been related to autoclave rupture disc failures of March and April of 1955 [15a].

"Continuing incidence of chloracne" was reported in September 1968 [8], when "an intensive investigation of possible sources of contamination" was being undertaken. Work was begun on correction and alterations of "pollution and safety problems" in the area [9a].

According to Homer Smith, the incidence of chloracne at the 80 Lister Avenue plant increased between his arrival at the plant in 1952 and his departure in 1969 [9b]. Eugene Bak noted that chloracne persisted even after the introduction of the carbon purification tower [9c].

4.1.2 Dioxin Levels

As reported in I.T.'s "Site Evaluation, 80 Lister Avenue," 29 of 29 samples obtained in the "process building," where TCP operations were centered, were reported to contain dioxin between 2.7 and 1580 ppb. The next highest levels of dioxin were reported in the "chemical manufacturing building," where 27 of 28 samples contained .93 to 1280 ppb [10].

4.1.3 1960 Explosion

An explosion occurred on February 20, 1960, when rising pressure resulted from a runaway reaction in the autoclave during the manufacture of NaTCP. The explosion itself reportedly occurred from the sparking of a flying piece of metal which ignited methanol fumes [2,11]. The temperature in the autoclave had risen rapidly to at least 150°C [12]. The amount of dioxin that would have been released in the explosion would have depended upon the actual temperature in the autoclave, as heat tends to promote dioxin formation [13].

A newspaper article relates the hurling of "large slabs of concrete" and "steel drums" as a result of the explosion [14]. Depending upon the contents of these drums and the degree of disturbance of such surroundings as the discharge pit and the concrete storage pad on the riverfront, this would have been another route of dioxin release.

4.1.4 Other Potential Sources of Discharge

There are reports of several rupture disc releases. These releases were safety features resulting from an excess in pressure in the autoclave. Besides the explosion of 1960, rupture discs reportedly blew in March of 1955 and on April 8, 22, and 23 of 1955 [15a]. The failure of a water pump, which circulated cooling water through the autoclave jacket to control the reaction temperature, also resulted in a rupture disc release in September 1958 [12].

Homer Smith's deposition noted several (more than five) rupture disc releases in which gases, possibly with entrained liquids, were released from the autoclave [15b]. One release after the reconstruction which followed the explosion occurred while the ground was covered with snow. Smith was then able to trace the trail of discharged materials into and beyond the Sherwin Williams parking lot, which was next to the 80 Lister Avenue site. This discharge shows one possible means by which dioxin-containing materials could have traveled beyond the 80 Lister Avenue site.

These rupture disc releases would have discharged some of the contents of the autoclave [16]. When these discharges occurred, material would have been released to various on-site locations such as the atmosphere [17], the river [19a] (through a pipeline), and possibly a pit [18]. Burton's recollection of the autoclave in the 1950's indicates that autoclave discharges may have been directed at the river [19a], while Heisele noted that, in the 1960's, a pressure relief valve on the autoclave was followed by a secondary rupture disc

[19b] and that the autoclave blow line would have discharged emergency releases above roof level [19c]. After 1960, the autoclaves were between the process building and the river, where there was a concrete bunker "in which the autoclave sat" [19d]. Pre-explosion (1960) autoclave operations took place inside the process building [19e].

Another potential problem area in terms of discharge was tank No. 137, the TCP intermediate storage tank. A September 1968 report relates the removal of this tank from the system except for use as an overflow catch tank [20]. The November 1968 report notes the planned removal of this tank, which reportedly presented "both a pollution and safety hazard" [21a].

There were, according to Bak, leaks in the TCP unit [21b]. Leaks were reported in the TCP acidification tank pump-out line [21c] and in the gasket of the TCP recovery unit [23]. The TCP recovery tank was a source of other possible discharges of dioxin-containing materials. A "burp-over" of hot water in this unit, which acidified liquid from the "T" process after filtration, was noted in Kennedy's deposition [22]. This hot water reportedly "could possibly contain dioxin." In addition, typical losses of TCP from the TCP recovery unit reportedly might have been around 0.2% due to solubility of TCP in the acid-water [24]. Discharge of these wastewaters would have been a route for dioxin release, since wastewaters were sometimes reclaimed and sometimes discharged (see Section 4.8, WASTEWATER).

A pinhole leak in a weld on a fitting on the top head of the autoclave was described by Burton. The repair of this leak was reported to have alleviated the rupture disk problems at the time [25a]. Leaks on an autoclave also reportedly occurred when operations resumed after the 1960 explosion [25b].

Burton described a carbonaceous residue in a lab autoclave batch after overheating the batch to 210°C. How much residue, if any, accumulated during normal autoclave operation is questionable [7].

Burton's deposition, however, does indicate that the autoclave was occasionally flushed [129a]. Further reference to autoclave flushing is contained in other depositions [129b, 129c, 129d, 129e, 129f] which state that the autoclave was flushed with methanol, caustic [129c] or water [129f], and that washwater could have been discharged to the river [129e]. In addition, as a consultant, Burton's instructions for operation of the autoclave included its rinsing with 750 gallons of water after a batch was completed and draining this water to the sewer [26a]. These statements indicate that dioxin-containing materials were likely released into the environment due to autoclave flushing.

Dioxin-containing materials would likely have been lost when "residual material" containing TCP was reportedly discharged in the flushing of process piping and equipment [26b]. The steam-blowing or disconnecting of lines (see Section 4.3, General Process Equipment Leakage) when TCP lines plugged [26c] also probably contributed to the loss of dioxin-containing materials.

Another means for release of dioxin-containing materials was the disposal of the excess salt and contaminants which were shoveled from NaTCP storage tanks [26d]. Since salts were water-soluble, they were probably dumped into the river [26d].

4.2 2,4,5-TRICHLOROPHENOXYACETIC ACID (T) AREA

Discharges from processing operations in the "T" area would have occurred as follows:

- Plugging of pumps with "residual construction debris" and plugging of lines;
- Fume exposure at a manhole at the T reactor;
- Fume emissions and product discharges in the flaking of T acid;
- A leak in the reslurry tank;
- A leaking settling tank;
- Leakage in "product" lines and transfer lines;
- Molten acid going overhead in the Luwa dryer;
- Structural failures of the T mother liquor acidification tank and the glass-lined dry acid receiver;
- "Housekeeping" and equipment problems in the ester area;
- Washwater discharge in Butyl-T washing;
- Centrifuge fume exposure and washwater discharge.

4.2.1 Dioxin Levels

Dioxin levels in the manufacturing (D and T production) building as reported in I.T.'s "Site Evaluation, 80 Lister Avenue" ranged from 0.93 to 1280 ppb with 27 of 28 samples testing positive for dioxin. In addition, 9 of 12 samples obtained by I.T. from process vessels and outside storage tanks contained dioxin [10].

4.2.2 Facility Expansion

The acid manufacturing building underwent an expansion in the 1960's. Demolition and site preparation were scheduled to begin on October 17, 1966 [27]. The expansion included facilities for the purification of TCP and for the flaking of T to replace the production of the old wet cake product. The expansion also included the addition of a warehouse [2]. On July 4, 1967, the T unit reportedly was shut down so that the area could be turned over to construction of the new D unit. On September 18, T acid production was resumed in the modified old D unit [2].

Problems reportedly occurred in the startup of the T unit. These problems included the plugging of lines. Pumping difficulties, which "seemed to be due to trash remaining from construction plugging the pumps," were also troublesome [28]. Operational errors and continued plugging of lines were reported in October [29], and operations reportedly improved in November [30]. If process wastes were greater than normal at this time due to the noted process failures, dioxin-containing materials would likely have been discarded.

Another possible source of dioxin release would have been the expansion. During this period equipment was being moved, modified and replaced and construction was underway. However, detailed information about the modifications and construction, as well as the means of transport and disposal of materials, was not provided in the depositions.

4.2.3 Vapor and Particulate Emissions

A certain amount of fume exposure was reported in the John Burton deposition as being associated with the T process. Burton noted a manhole at the T reactor which was a source of fumes [31]. Product quality control sampling through this manhole was achieved by reaching through the manhole and scooping out some of the contents of the reactor [32,32a]. This sampling would have occurred about 2 to 3 times in a 24-hour day [32a.] Workers in the T area were among those who had chloracne, according to Bak's deposition [32b]. Since chloracne has been associated with dermal exposure to a group of chlorinated compounds which includes dioxin, this report of chloracne is a likely indication of dioxin release since it suggests that operations personnel were able to come into direct contact with dioxin-containing materials.

An odor problem was also reported in November 1968. The "odor problem in the area" was reportedly "worse when flaking 'T' acid than on 'D'" [33a]. An odor problem could be indicative of poorly controlled air emissions of the T acid which would have likely carried with them dioxin. "Open" vessels in the T area included the filter and the centrifuge [33b].

4.2.4 Operations

In October 1967 the reslurry tank, which had reportedly been leaking, was replaced with a new tank, eliminating a major problem in the operation of the unit [29]. An October 1968 report noted that the pump to the reslurry tank required replacement because of corrosion failure [34]. Leaks from the reslurry unit, which facilitated the pumping of Na 2,4,5-T, might have resulted in a release of dioxin-containing material.

Leaking in the settling tank, in which Na 2,4,5-T precipitated in water upon cooling, was reported to have been found in November 1967 only about three weeks after it was patched. It was decided to purchase a new vessel to replace it [30a]. Other leaks that have been reported have included the slurry tank "leaking badly when slurry got thin upon heating" [30b], "numerous leaks" in the stainless steel transfer line from the settling tank to the sodium sulfate makeup tank [30c], and "numerous product line leaks" [30d]. Such leaks could also have been a point of release of dioxin-containing materials.

Attempts to dry 2,4,5-T in a Luwa dryer reportedly resulted in "molten acid going overhead" in April 1968. This had reportedly occurred in the previous September [35]. These discharges may have been a source of release of dioxin-containing materials. In May, attempts to dry the acid with the Luwa were abandoned in favor of batch drying. In this operation, frequent plugging of the lines occurred between the dry acid receiver and the flaker [36]. Piping was on occasion reportedly replaced to eliminate plugging problems

[36a]. When product streams plugged lines, piping had to be disconnected and reassembled [36b].

A September 1968 report [37] related the failure of the T mother liquor acidification tank. The 200-gallon glass-lined body, the agitator, and the speed reducer were lost [37]. In December 1968 the primary acidification tank was prepared for service again. Also, the glass-lined dry acid receiver was being repaired, as it had a hole through it to the jacket [38]. Dioxin may have been released in the failure of these vessels, depending upon the nature of the failures.

Gordon Steward, in his deposition, reported that the 2,4,5-T acid was stored in carts as it was collected from the centrifuge [39a]. The nature of the transfer of this acid, which was in the form of a slightly wet white powder, has not yet been discovered, so that the corresponding potential for spillage is not established. Shoveling or dumping of cart contents may have occurred, resulting in spillage and exposure to dioxin-containing materials.

Flaking of T-acid also resulted in likely releases of dioxin-containing materials. Bak stated in his deposition that material was around the flaking unit, and sometimes on the floor or on the machinery [39b]. This seems to correlate with the reported odor problem in the flaking area [33a].

A lost-time accident resulted when an operator shutting down the flaker was splashed with molten acid [39c]. Such discharges would have contributed to the release of dioxin-containing materials into the environment.

Process wastewaters would also be expected to carry with them some dioxin [see WASTEWATER]. An example of this wastewater release was the wastewater from the washing and scraping of the centrifuge, which was likely discharged to the river for a period of time in the 1950's [39d].

4.2.5 Esters

Burton's deposition noted that a worker at an ester unit had chloracne [40]. Maintenance problems were reported as of 1968, and equipment replacement was called for because of poor arrangements and high maintenance requirements [2]. An example of these problems was an esterifier which was out of service with a bad break in the expansion section of the jacket [41a]. Also, breaks in several glass-lined vessels were noted to have occurred in the ester unit [41b], and failures of hot melt tubes reportedly occurred in ester lines [41c, 41d]. These repairs would out of necessity cause piping and apparatus to be disconnected, potentially resulting in a loss of products and intermediates.

Smith's deposition described the ester unit as a "housekeeping" problem, with material on the floor from time to time [41e]. The ester area was described by Steward, in his deposition, as being more wet than other areas [42]. Steward attributed this mostly to water and possibly to some residual alcohol from decantation. Release of ester-related materials is an indication that dioxin-containing materials may have been discharged.

One of the chemicals produced at the Newark plant was Butyl-T ester. A report dated June 1968 noted that washing of this ester was started to meet product specifications [43]. The washwaters might have contained some dioxin, and their discharge or reclamation would pose a potential source of dioxin release.

4.3 GENERAL PROCESS EQUIPMENT LEAKAGE

Discharges in piping and other process equipment would have occurred as follows:

- Leakage of pipes;
- Disconnecting and flushing of pipes;
- Leakage of valves, flanges and seals.

According to the depositions of former Diamond Shamrock plant personnel, leakage was a common occurrence at a chemical plant [44,45], and did, in fact, occur [46,47,48a,48b,48c]. While the deponents had little or no recollection of any particular spill or leak situations, suggested examples of such situations were overpumping into tanks and leaking of pipelines [49]. The most likely places for leakage at a chemical plant were noted by Heisele to be valves, flanges, and seals [49b], and leaks in pipes were noted by Burton as a means for chloracnogen transport [49c]. Chonoles, in his deposition, indicated that, based on his knowledge of the operation of the Lister Street plant, leaks from pipes and process equipment were the most likely source for dioxin getting out of the process and into the area of the Lister Street plant [49a].

A department of health visit in 1963 resulted in a list of recommendations which included the repair of leaks and leaking valves [50]. Deponent Guidi recalled no such leaks and surmised that the memo may have been a standard recommendation. However, an April 1963 medical report noted chloracne and acquired porphyria in a plant employee who had seven years of service and whose job it was to weld leaking vats [51a]. This is an indication that leakage did occur.

Another indication of leakage is information in depositions and operating reports which notes that lines were frequently plugged [36a, 36b]. Piping was probably at some point discarded but this was rarely done as piping was recycled when possible. If unplugging with steam was impossible, then the pipe would be disconnected [51b]. Pipe cleaning wastewaters, which would have likely contained some dioxin-containing material, would have gone to a sewer leading to the river, to the industrial sewer, or to the floor where it would have been washed down. Floor washdown water may have gone to the river [51c]. The disconnecting and reassembling of pipelines would thus have caused losses of materials which likely contained dioxin. Piping and other wastes were stored in areas open to the air [51d] resulting in further exposure to the atmosphere of dioxin-containing materials by wind, rain, movement, etc.

Besides the general indication of the depositions of Messrs. Steward, Kennedy and Burton [44,46,47,48a,49a] that leaks indeed have contributed to discharge of materials that likely contained dioxin, other leakage or discharges probably occurred in units including the TCP autoclave, the anisole still, a TCP intermediate storage tank and the 2,4,5-T pumps and piping [See Section 4.1: 2,4,5-TRICHLOROPHENOL PROCESS; Section 4.2: 2.4.5-TRICHLOROPHENOXYACETIC ACID AREA, and Section 4.4: PUMPS]. This information seems to indicate that, over a period of years, leakage and discharge related to typical plant operations likely contributed to the release of dioxin from the process.

4.4 PUMPS

Discharges in pumping would have occurred as follows:

- Pump damage and subsequent discharges due to problems in 2,4,5-T transport;
- Ruptures of pump seals.

In his deposition, Robert Chonoles indicated that dioxin could have escaped by a rupture of a pump seal [52]. In addition, F.G. Steward indicated that there was leakage in some of the pumps in the 2,4,5-T area [53], while F.R. Kennedy noted the same problem, where 2,4,5-T crystals chewed up gears in pumps [54]. This leakage was in the form of 2,4,5-T, which quickly solidified and was evidenced around the affected pump area in the form of a cake.

Burton noted that pump leaks were common in the 1950's, especially since pump designs were not yet very refined [55c]. He also noted leaks in pump packing glands as a means of chloracnogen transport [49c], and pointed out that plugged pumps were generally blown clean with steam [51b].

Steward noted "centrifugal pumps in the general class" [53], while F.R. Kennedy described gear pumps which were problematic and which were replaced in the new T unit. Steward also talked about problems with the pumps to the amine reactor [55a], and an Operating Report [55b] noted that "pumps and mechanical seals remain a maintenance problem." Thus, pump problems were a continuing difficulty at the 80 Lister Avenue plant.

In light of the information supplied by the deponents, it seems that leaks and failures in pumps contributed to the release of dioxin-containing material.

4.5 DISTILLATION

Discharges from distillation operations would have occurred as follows:

- Flushing of residue from the stripper;
- Waste water discharge from the anisole stripper;
- Anisole condenser tube leakage problems;
- Sample spillage around the anisole sample tap.

According to EPA's publication "Dioxins," high concentrations of dioxins have been found in toluene still bottom wastes in TCP production [56]. The documents and records reviewed by PS&S have not indicated that this process step was performed at the Newark Diamond Shamrock plant. However, two other distillation steps were performed in the Diamond process. The first of these steps was a methanol distillation from the autoclave and a redistillation in a crude methanol still. The second step took place in the stripping unit, in which steam distillation was used in recycling anisole [2].

An outbreak of chloracne in May and June of 1955 occurred several months after the anisole step was introduced into the process [6,7]. While this outbreak may have been related to the autoclave rupture disc releases of March and April 1955, the introduction of the stripping process to replace the dilution/filtration process was suspected to have been a factor in the reported chloracne problem [57c]. Later testing indicated that filtration did remove much of the dioxin in process streams [57e]. A 1968 sample of recovered trichloroanisole showed 73 ppm dioxin [57d], indicating that discharges from the stripping unit might likely contain dioxin.

Burton noted that the residue from the stripper, which would have consisted of accumulated salts and water, was sometimes flushed to the river [57a, 57b]. This would be a likely source of release of dioxin.

"A discharge of salt cake from this still resulting from the use of new spargers caused plugging," but this was reportedly not believed to be a serious problem [58a].

Some vapor was released from the steam stripper. No testing for chloracnogens was performed on the stripper overhead water layer, according to Burton, or on the stripper venting system [58b].

The first recycle of organics at the plant reportedly took place in December 1956 [1]. Burton indicated in a set of 1967 operating suggestions which he developed as a private consultant that 1 in 20 batches of charge to the autoclave should be anisole since 5% of the tetrachlorobenzene feed was recovered as anisole in each batch [59].

Burton, in his deposition, stated that the waste water from the anisole stripper was routed to the river [60a, 60b]. This would have been after the separation of the anisole from the condensed steam. This handling of materials would have resulted in some discharge of dioxin-containing material since dioxin was found to have carried over in recovered anisole [57d].

Burton also noted that the anisole condenser, which was probably vented outside the building, would have caused emissions to the environment possibly containing dioxin [60]. In addition, dioxin could have been released as a result of a small amount of discharge in the form of sample spillage around the anisole sample tap [61a]. Samples were reportedly drawn from the anisole still about a quart at a time [61b].

Operating reports by Diamond plant personnel in 1968 and 1969 indicated ongoing problems with the anisole still condenser tubes [62,63,64]. The leaking condenser reportedly contributed to higher than normal TCP raw material consumption in June 1969 [63] and adverse effect on production in November 1968 [65]. Depending upon the nature and extent of the leakage, there would have been fairly

4.6 FILTERS/CENTRIFUGES/PURIFICATION

Discharges from filtration, centrifuging and purification would have occurred as follows:

- Quality control sampling of filter cake;
- Filter washwater and spent filter cloth disposal;
- T centrifuge fume exposure;
- Scraping and washing of the T centrifuge;
- Sewering of acid which was used to regenerate the carbon purification column.

4.6.1 Filters

John Burton's deposition indicated that, until 1954, the TCP was acidified so that it would be retained as a solid in an open filter which was shoveled out [66]. This conflicts with a report by James Worthington (Diamond Shamrock) that the NaTCP passed the filter as a liquid [1] and that other impurities, which at that time would have included trichloroanisole and unreacted tetrachlorobenzene, were retained as solids. Worthington suggests that dioxin would have been trapped in the filter cake, while Burton's analysis seems to suggest that the bulk of the dioxin would have remained in the process.

A steam-stripping step was introduced in 1954 to replace the old filtration method [1]. This stripping method allowed for the recycling of trichloroanisole. Leakage from the stripper was a possible source of discharge of dioxin-containing material. (see Section 4.5, DISTILLATION).

The T filter also was an open filter, but it was replaced with a rotary filter in 1955 [67]. The T and TCP "open" filters, as well as the T rotary filter, were all open to the atmosphere, but, as Burton described in his deposition, there may have been little fume exposure because of the chemical and physical state of the materials being handled [67]. Losses of materials in handling because of the open nature of the system and operations were, however, possible. Furthermore, a 1967 scrubber alteration permit application noted slight losses from batches just before and after filtration [86], indicating that release of dioxin-containing material could have occurred.

Another filter which reportedly existed in the process was a Monel screen filter. This filter screened the salts from the NaTCP stream leaving the anisole still [2]. Kennedy's deposition related the "casual dioxin contamination" of the sodium salt filter, which was occasionally sampled by having a piece of the cake broken off by a worker [68a]. Worthington's report indicated that the salt recovered in the filter was dissolved in water for disposal in the industrial sewer [1]. Burton's deposition states that no filter existed in the TCP process after 1954, after the introduction of the anisole still [68b], but this may well have been installed after the 1960 explosion.

Evidence of any leakage or failures of the filters was not acknowledged by any of the deponents. An important factor in assessing the potential for dioxin release, however, is the filter washwaters. According to Burton, some of these washwaters were recycled and some were discarded to the sewer or to the river [69a,69b]. References from other depositions corroborate Burton's recollection, adding that washwaters may have gone to a sump [69c]. These washwaters would be expected to have contained some dioxin.

In addition, potential for discharge of dioxin-containing material existed in handling, sampling and the disposing of the filter cake and in the replacement and disposal of filter cloths [69d]. All solid wastes were reportedly hauled off-site by a contractor, Mr. Nick Toscano [1], but facts about the intermediate steps of physical transport and possible storage have not been discovered.

4.6.2 Centrifuges

The T centrifuge was noted in Burton's deposition to be a source of fume exposure in the plant [70], even though it was vented to a scrubber. This centrifuge was sometimes scraped and washed, according to Burton [71]. This scraping and washing operation appears to have been a source of dioxin release, to either the river or the sewer.

Before Diamond Shamrock started buying its tetrachlorobenzene in the early 1950's, a part of its process included a tetrachlorobenzene centrifuge, which separated solid tetrachlorobenzene from liquid process stream components. The centrifuge, which was manually emptied, was suspected as a source of chloracne in the short time that tetrachlorobenzene was being produced by Diamond Shamrock [72].

4.6.3 Purification

Experiments for the purification of TCP were performed with filtration and with a carbon column [73a]. The old dilution/filtration process of separating organics and impurities was apparently "trouble-free" [57c]. Indeed, it was discovered that filtration could drastically reduce the level of dioxin in process streams [57e]. Bak, in his deposition, states that dilution/filtration was attempted before the carbon column was installed, but that it did not result in the reduction of dioxin levels that was thought possible [73c]. The carbon column was thus chosen to purify TCP, with the pilot column (test column) running substantial volumes of TCP for the first time on September 27, 1967 [2]. A secondary filter removed slight amounts of solid carry-over from the column [73b], with the effluent TCP running at about 1 ppm p-dioxin [74]. Again, this filter appears to have been a potential source of dioxin discharge with the amount released depending upon the handling of the filter cake.

A permanent tower was installed in July of 1968 [75]. Both the pilot tower and the permanent column were periodically regenerated with acid [76,77,78]. This cleaning resulted in a "burp-over" of acid out the vent [76]. This may have discharged some dioxin. The permanent tower had once had its carbon replaced when acid cleaning had not sufficiently regenerated it [79]. The spent carbon was reportedly drummed without any spillage with no details provided of its disposal site.

The acid used to regenerate the column was reportedly sewered [80,1]. A report on tests performed to analyze the regeneration of the column showed approximately 0.2 grams of dioxin to have desorbed from carbon in the acid and rinses tested [81]. Thus, acid discharge from the carbon column appears to have been a source of dioxin release, with the amount exposed to the environment contingent upon whether the acid was drained through floor trenches, pumped to a sump pit, etc.

4.7 VENTS/SCRUBBERS/AIR EMISSIONS

Dioxin-containing releases related to vents and scrubbers would have occurred as follows:

- Air emissions from the TCP building exhaust fans and vents that were open to the atmosphere.
- Fumes from the centrifuge;
- Organic materials lost with water vapor leaving the T reactor;
- Slight losses from hot batches just before and after filtration;
- Vapor losses from acidification;
- Dust formed in the flaking process;
- "Problems of contamination emitting from the various vents of the TCP unit;"
- Poor venting at the TCP intermediate storage tank;
- Poor venting at the anisole still;
- Discharge of scrubbing tower effluents;
- Reduction of pressure with associated vapor releases from the autoclave after each batch.

According to EPA's "Dioxins", dioxin vapor pressure is low. However, water-mediated evaporation of dioxins reportedly may take place [82], indicating that dioxin may be transported in the vapor phase. Dioxin tends, however, to bind to solids: it binds firmly to soil and may become concentrated in certain types of residues [56]. Thus, emissions of particulates to which dioxin is bound is a possibility.

Some information about process vents and scrubbers has been provided in the depositions. Burton's deposition provides some information about venting in the plant in the 1950's. Burton notes that the centrifuge was vented but was still a source of fumes in the plant [83a]. A plexiglas hood was reportedly installed on the centrifuge at some point to collect fumes [83b]. Burton also relates that the T reactor was vented to a scrubber [84], but that the anisole still condensor was vented to the atmosphere [60]. He describes vapors from tanks and spillage from sampling as a means for chloracnogen to transport [49c]. Burton also states that the venting of autoclave pressure to outside of the building at the end of a batch was a means of chloracnogen transport [49c]. This venting would likely have released vapors and possibly some traces of liquid which contained dioxin, and based on Diamond Shamrock operating reports from the period March 1966 to July 1969 [134], would have occurred an average of 58 times per month.

Chonoles' deposition indicates that there were two scrubbers on the property [85a]. Meanwhile, depositions indicate that, while the acid building (D and T) was serviced by a scrubber, the TCP building was simply ventilated by 40" exhaust fans [85b,85c]. This situation reportedly existed for a period of time in the 1950's and maybe longer, and indicates that dioxin-containing materials may have been released through air emissions from the TCP building.

A 1967 permit application was filed for alterations of the scrubber system. The permit lists the sources to the scrubber. These include some organic materials lost with water vapor leaving the T reactor and some slight losses from hot batches just before and after filtration. Also listed as sources were some additional vapor losses from acidification and drying, as well as some dust formed in the flaking process. This same application provided the information that emissions of NaTCP mist without a control unit would have been 1.2 pounds per hour, while controlled emissions were 0.06 pounds per hour [86].

Steward indicated that this scrubber system was in place since 1963, and that the 1967 permit was for alterations related to the expansion undertaken at that time [87a]. A Diamond Shamrock report by

James Worthington states that "all vents were inside the process building until the late 1960's." By that time, organic particulates were controlled to 10 pounds per day, by a 2000 SCFM 7-ft. Peabody caustic scrubber [1]. Worthington's comments regarding process vents seems to contradict Heisele's deposition, which states that nothing was released into the building and that some process vents discharged to the atmosphere [87b].

There is further evidence of some pollution and safety problems in the plant's vent system. "Problems of contamination emitting from the various vents of the TCP Unit" were noted in a November 1968 report. This report states that "work orders were issued to connect the intermediate storage tank vent to the anisole still, eliminating this source of contamination." Plans were "being drawn up to improve the venting arrangement at the anisole still rupture disc, and also at the anisole receiver and drop tank" used for anisole storage and transport [88].

By January 1969, the vent changes at the TCP intermediate storage tank were reportedly completed. The report notes the request for the installation of an automatic cutoff on the steam supply to the anisole still, and for additional vent changes. Both of these changes were "designed to minimize the discharge of organic fumes to the atmosphere" [89]. This information indicates not only that emissions did occur, but also that, after design changes, emissions continued at reduced but non-zero rates.

Scrubbing tower effluents were, according to Kennedy, discharged into the sewer [90]. Scrubber effluents may also have discharged to a pit near the river [114a,114b] and/or to the river before the sewer existed. Consequently, since scrubber effluents likely contained dioxin, and because some fume and pollution problems apparently existed around the TCP and T units as described above, the vent and scrubber system should be considered a potential source of release of dioxin-containing material.

4.8 WASTEWATER (GENERAL)

Discharges of dioxin-containing material in wastewater would have occurred as follows:

- Discharge of 100 tons of unrecycled 2,4,5-T effluents per year into the Passaic River as of 1959;
- Overflow of waste TCP streams from a sump to a sewer;
- "Tower upset" acid dumps;
- A chlorination area outfall;
- Liquid discharges to floor drains.

Diamond Shamrock began process operations at the 80 Lister Avenue plant in 1951. Process wastewaters were discharged to the Passaic River prior to the 1956 construction of a sewer in the area of the "D-building," where D and T acids were manufactured. After the construction of the sewer, wastewaters from the TCP process would have been transferred to the sewer system or would have been discharged into the river [91].

The Army Corps of Engineers cited the plant for hydrochloric acid discharge in the days of Kolker ownership [92]. Later, the Sewerage Commission spotted a leak in an alcohol pump which discharged into the river, precipitating the installation of the sewer in the D-building [93]. The plant was also cited in 1968 for sulfuric and hydrochloric acid discharges [1].

Further detail relating to process wastewaters is included in a 1960 John Burton memo [94]. Burton notes the discharge into the Passaic River of about 100 tons of 2,4,5-T effluents per year. These effluents included trichlorophenols and some T-acid and esters. The acids discharged to the river, some of which may have been used in the TCP and T processes, totaled 2000 tons in 1958 and 4400 tons in 1959. Burton, in his deposition, describes some of the sources of this wastewater. The washing of esters [95] and filters [96] resulted in the discarding of some of the effluents which were not recycled. Burton stated that everyone (involved in plant operations), except for maybe secretaries, knew about the discharge of large amounts of chlorophenols into the river [97a].

A Diamond Shamrock report [1] described the origin and destination of process wastewaters. The report lists aqueous sodium chloride and sodium sulfate as TCP process wastes, as well as the aqueous condensate from the anisole stripper. Rerouting of the sodium sulfate overflow line [97b] due to the hazards of river pollution was reported to have been done in 1966. Based on this information, prior to that date, dioxin-containing materials could have been discharged to the river through this line. The acid used in the TCP process was believed to have gone to a sump with the overflow discharging to a sewer (after 1956). The Diamond Shamrock report [1] notes 30,000 gallons of wastewater per day, "one-third of which may have contained some dioxins."

F.R. Kennedy in his deposition talks about muriatic acid that was dumped into the river during absorption "tower upsets" [98]. Kennedy also notes an outfall to the river in the chlorination area [99], and further states that potential liquid discharge would have gone to floor drains [100]. In addition, he discusses the possibility of "natural drainage" as a means of liquid waste transport [101] and notes an open trench to the river's edge that connected with the floor trenches [102].

Steward, in his deposition, describes an outfall to the river from cooling water and from acid from the drying columns [103]. Guidi recalled the discharge of sodium sulfate and a small amount of T-acid discharge into the sewer [104], while Chonoles remembered acid discharges into the river [105,106].

A 1969 study of flow in the main Diamond Shamrock industrial sewer showed 400 gpm (gallons per minute) against a maximum of 500 gpm. Discharge of spent sulfuric acid, that Diamond Shamrock couldn't use, to the industrial sewer was reportedly decided to be a satisfactory means of correcting part of their "water pollution problem" [107].

It appears, based on the deponent's statements, that large volumes of liquid wastes associated with the TCP and T processes were discharged into the river and the sewer. Much of this waste could have carried with it some dioxin. Some of the means by which the dioxin would have been carried are by solubilizing in organic wastes and/or acids and by binding to particulates that may have been discharged in wastewater.

According to I.T.'s report "Site Evaluation, 80 Lister Avenue" [10], 26 of 36 Passaic River sediment samples contained 0.53 to 130 ppb dioxin. Dioxin contamination reportedly increased with depth.

4.9 SEWERS AND SUMPS

The following discharges, were likely routed to a sump before release into the sewer or the Passaic River:

- Discharges from the TCP area (See Section 4.1);
- Sulfuric acid discharges from the scrubbers (See Section 4.7);
- Process stream discharges related to the anisole stripper (See Section 4.5)
- Ester process effluents;
- Chlorophenolic wastes.

The depositions of the former Diamond Shamrock employees contain various pieces of information relating to the location and contents of sump pits at the plant site. A sump existed at the sewer location in the area of the D-building [108,109a], serving as a collection point for materials before they were discharged into the sewer. Open grating covered the trenches that led to this sump, in which solids separated from the liquid that went to the sewer [109b]. Before the installation of the sewer, these trenches led to the river [109c]. Most chlorophenolic wastes were discharged to the sewer after 1956, when the sewer was installed [109e]. These wastes would be expected to contain dioxin.

Kennedy recalls an additional sump and notes that both sumps were concrete-lined [110]. Diamond Shamrock tests reported in 1968 that the additional pit showed 75 ppm dioxin [111a]; the contents of this sump pit were reportedly related to the anisole stripper. This additional sump pit may have been the one reported by deponents to have been in the TCP area [111b, 111c, 111d, 111e]. This sump may have received waste cooling water [111c] but also may have received liquid wastes and wash waters [111b]. Also in the sump pit were, according to Kennedy, process streams, dirt from the ground, and rainwater [112].

Other deponents indicate that there was yet another sump pit [113], and that some of the material that went out to the pit(s) may have been emergency discharges from the TCP area [103] and sulfuric acid from scrubbers [114a,114b]. Bak's deposition noted that most of the sumps "act as a seal for the piping that came under the water and the surface of the water," sealing "any vapors that would be coming off" from being exhausted to the atmosphere [114b].

"Shoveling" (cleaning) of the sump pit that led to the industrial sewer occurred at least once a year, and probably several times a year; Burton described this cleaning as a "dirty, messy operation" [109d]. The TCP pit was also occasionally cleaned out, according to depositions [111d, 111e]. Any unrecycled wastes from the sump pits would have been packaged in metal or fiber drums. These drums were waste drums from raw materials which would have been covered if people involved in the operation "had covers convenient" [109d]. Reportedly, most solid wastes were hauled to the Hackensack Meadowlands [131d].

Other noted characteristics of the pits are a possible outfall to the river [103] and the discovery of chloracnogens, which were materials that were tested and found to cause chloracne, in the sump line [115a]. This sump line was a trench that ran through the acid building [115a]. The presence of chloracnogens indicates that dioxin-containing materials were being released from the process.

Before the industrial sewer was installed, ester unit effluents were reportedly being released to the sanitary sewer. Diamond Shamrock was told by the City of Newark to stop these discharges, as the odor problems caused by these releases were present "throughout the lower part of Newark" [115b]. These discharges would likely have caused releases of dioxin-containing materials into the environment.

A Diamond Shamrock report [1] indicates that a sump may have removed the dioxin from acid waste streams before they went to the sewer. Because of the exposure of the pits to materials which likely contained dioxin and the reported messiness of the sump cleaning operations, they should be considered a likely source of dioxin discharge.

According to I.T.'s report "Site Evaluation, 80 Lister Avenue," the silt beneath the fill in the northern portion of the site showed low-level dioxin contamination and all of twelve sewer and sump samples were found to contain dioxin in concentrations ranging between 19.5 and 9160 ppb. I.T.'s report lists, besides the two sumps in front of the process building, six other sumps that were sampled.

4.10 SAMPLING/QUALITY CONTROL

Dioxin discharges in sampling and quality control operations would have occurred as follows:

- Discarding of unused or wasted samples;
- Spillage at the anisole sampling tap;
- Fume exposure in sampling the 2,4,5-T reactor.

F.G. Steward, in his deposition, states that samples were taken in each stage of production [116]. Raymond Guidi notes sampling at the autoclave and the steam stripping unit [117a]. Sampling valve(s) existed at the autoclave [117b], and each autoclave batch was reportedly sampled [117c]. T reactor sampling would have occurred 2 to 3 times in a 24-hour day [32a], while esterification batches were sampled about once an hour [32c]. Diamond Shamrock retained certain samples for a period of time in a designated storage area [118].

Unused samples may have been discarded. Valuable samples of product were to be returned to the process [119]. The discharge or disposal of unused or wasted samples could have been a source of dioxin release, as could the small amount of spillage associated with sample drawing. An example of spillage that was reported to have occurred is at the anisole still tap [120a]. Also, fume exposure at the manhole at which the T reactor was sampled [120b] was a source of exposure to process streams [5a] and possibly of dioxin transport. Burton, in his deposition, noted fume exposure and possible spillage in sampling as a possible means for chloracnogen transport [49c].

4.11 PACKAGING/TRANSPORT

Discharges from packaging and transport operations would have occurred as follows:

- Dust in the "bagging" area;
- Discarding of "gunk from tanks" during plan shutdown;
- Truck traffic as a potential means for dioxin-contaminated dust migration;
- Spillage from loading or transport.

According to Burton's deposition, storage tanks, tank car loading, and NaTCP loading to railroad siding all took place in ground areas, while storage of NaTCP and 2,4,5-T was in building areas [121a]. Smith, however, indicated that there were raw material and finished product storage tanks outside [121b]. While most of the plant was reportedly blacktop or concrete-covered, there were reportedly storage tanks for raw materials and possibly other materials, as well as a parking lot in dirt areas [121c, 121d,131f]. Any spillage in loading or transport in these areas would thus have gone into the ground and onto dust and dirt. Container sizes ranged from 1-gallon to 55-gallon drums.

Esters and amines were sold as liquids, as was NaTCP in water solution [122]. T acid was sold as a solid, in lever packed drums [123] and/or craft (paper) bags with liner [124]. Steward, in his deposition, stated that there was dust in the "bagging" area [125]. This dust, which likely became to some degree airborne, was a likely source of dioxin transport.

During plant shutdown, finished products and raw materials were shipped to the Diamond Shamrock Des Moines facility. Other hazardous chemicals, such as "gunk from tanks," were discarded [126]. This practice was a possible route of dioxin release, although details were not provided.

A means of possible transport of dioxin off the site was given in Richard Dewling's (EPA) letter to NJDEP Commissioner Hughey [127a]. In this letter, Dewling cited truck traffic as a means for dioxin-contaminated dust migration in the vicinity of the site. Trucks reportedly went past the parking lot in the south area of the site and onto other site areas [127b].

4.12 MAINTENANCE

Discharge of dioxin-contaminated materials as a result of maintenance and housekeeping operations would very likely have occurred as follows:

- Discarding and relocation of old pipes and debris during maintenance procedures, after the 1960 explosion, and after the plant shutdown;
- Flushing of residue from the stripping tank, autoclave, and TCP tanks;
- "Poor housekeeping" at the riverfront (drum and equipment storage on a concrete pad).

The plant shut down for maintenance each year. In this time period, inspection and maintenance were performed on such process apparatus as seals, packings, impellers, condensers, etc. On occasion, old pipes and debris were discarded [128]. The means by which they were handled and disposed of would have been a factor in the possible release of dioxin-contaminated materials.

Also noted as occasional potential maintenance activity is the flushing of the autoclave, TCP tanks, and stripping tank residues [129a]. Whether the wastewater from these flushings was discharged to the river or to the sewer system, this aspect of maintenance presents a likely source of release of dioxin, especially since dioxin is relatively non-volatile [130] and might tend to accumulate in certain residues.

A reference to "poor housekeeping" [131a] at the riverfront, where drums and miscellaneous equipment were stored on a concrete pad, would indicate further potential dioxin-related discharges, especially if rainwater or liquid seepage flowed off the pad or through any cracks in the pad. Improvements in housekeeping occurred, according to Burton, in 1955 following chloracne trouble [131b].

Scrap piping was picked up by a special contractor [131c], while most solid wastes were hauled by the regular contractor to the Hackensack Meadowlands [131d]. Smith described the scrap storage area as "some concrete but mostly we will call it dirt" [131e]. The west side of the main building and the parking lot were, according to Smith, unpaved [131f]. Runoff from the concrete pad along the riverfront, washdown water, and flushing water [131g, 51c] would have gone to the river in certain periods of the plant operations. The pitch of the blacktop was towards the river [131h], according to Burton, except further from the processing building where the slope may have been towards the railroad tracks.

Smith noted that "water washing from the river past the bulkhead" caused undermining which had to occasionally be filled [131j]. This undermining again indicates that dioxin-containing materials may have spread.

Floor washings occasionally occurred [132] at the plant. Residual materials very likely carried with them dioxin-containing substances. In light of Burton's comment that "operators tended to be sloppy" in keeping their units clean [133a], these washings, as well as possible equipment flushings, are possible sources of dioxin release. Further indications of release to floors of process streams, which would likely have contained dioxins, was the frequent patching of the floors [133b] which were old and were chewed up easily by product spills [133c].

Salvage companies aided in disassembling the plant following the 1960 explosion [133d]. All debris was reportedly moved from the plant site. The disassembling of equipment would have resulted in the release of some residual dioxin-containing materials and the movement and reconstruction could have disturbed areas, such as sump pits, where dioxin was likely present. After the plant shut down in 1964, Homer Smith took seven truckloads of equipment with him to Diamond Shamrock's Greens Bayou plant [133e]. Disassembling and movement of plant apparatus in this time period could also have caused the release of dioxin-containing materials into the environment.

5.0

ASSESSMENT OF POTENTIAL DIOXIN (2,3,7,8,-TCDD) RELEASES

5.0 ASSESSMENT OF POTENTIAL DIOXIN (2,3,7,8 - TCDD) RELEASES

According to I.T.'s report "Site Evaluation 80 Lister Avenue," an estimated 96.2 pounds of dioxin are present in the soil at the 80 Lister Avenue site. This discussion presents a general analysis of how such amounts of dioxin may have been released to the environment as a result of certain plant operations at the Diamond Shamrock plant at 80 Lister Avenue. Because of a shortage of physical data on dioxin and a lack of information regarding many facets of process operations, quantitative estimates are presented only to convey the estimated order of magnitude of releases of dioxin related to a particular area of the process.

One of the areas of dioxin releases is reportedly the rupture of discs on the autoclave. These ruptures occurred as a result of pressure buildup which could have been caused by such factors as a runaway reaction or a failure of proper cooling water circulation. References to six of these rupture disc releases, including the one that resulted in the 1960 explosion, have been discovered.

Based on the highest discovered TCP concentration of 140 ppm in a 100% TCP solution, the total amount of dioxin that would have escaped if all of the autoclave contents had discharged in each of the six rupture disc failures was less than two and one-half pounds. If the dioxin concentration had been higher or if additional emergency discharges from the autoclave occurred, the amount of dioxin that escaped would have been higher. Conversely, incomplete discharge from autoclaves or lower reaction temperatures would have resulted in lower amounts of dioxin discharge. The estimate of less than two and one-half pounds of dioxin released, however, is probably a high estimate based on available information.

Another source of potential discharge of dioxin-containing materials was the vent and scrubber system. To assess the potential dioxin releases through vents and scrubbers, the estimated dioxin concentration in organic particulate emissions was assumed to be 1 part per million (ppm). This assumption was made even though evidence of detectable dioxin levels in emissions from plant operations has not been discovered, and 1962 vent sampling reportedly turned up no suggestions as to eliminating chloracnogens (chloracne-producing compounds) in the plant.

Scrubber-related emission rates for the Newark plant were included in the 1967 scrubber permit application. Based on the 2.4 pounds per hour of organic emissions of "vapor" and "mist" discharges from the NaTCP and T areas which would have been released with no control, the dioxin released through particulate matter could have been up to 0.4 pounds of dioxin over the period of Diamond plant operation. The system did, however, have scrubbers as far back as the 1950's. When controlled emissions of 10 pounds per day of organic particulates that reportedly existed by 1969 are considered with the same 1 ppm dioxin assumption, the dioxin emission becomes 0.07 pounds over the period of plant operation.

These estimates are intended only to provide a feeling for the possible order-of-magnitude of dioxin discharge due to air emissions. Since the 1 ppm assumption has no documented basis, these numbers should be interpreted in a limited way. One of the interpretations is that, based on 50 ppm dioxin in materials emitted from the controlled "T" process and the uncontrolled TCP process, only 14 pounds of dioxin would have been released in the period of plant operation.

Wastewater was another possible source of discharge of dioxin-containing material. Based on the 1959 discharge of 100 tons of unrecycled T effluent into the river, and based on the assumed dioxin concentration of 1 ppm (1000 ppb), this wastewater would have discharged with it about four pounds of dioxin. Lack of discovery of actual wastewater dioxin concentrations precludes a more meaningful estimate of dioxin discharge in wastewater. Since there may have been an outfall to the river, much of the dioxin in wastewater may have resulted in the river sediment contamination noted in I.T.'s report as well as the contamination reported in site soils.

The 75 ppm of dioxin reported in the pit near the river was likely the result of autoclave discharges, scrubber effluent discharge, or anisole still releases. The dioxin may have tended to accumulate in site pits, as noted in Worthington's environmental report. Recycled anisole dioxin concentration was at one point noted as having 73 ppm dioxin. Since ongoing leakage problems were reported in the anisole still, this unit must be regarded as a probable point of discharge of dioxin-containing material, even though quantifying the potential release is impractical with the available discovered information.

Other sources of discharge of dioxin-containing material for which incomplete information has been discovered are the flushing of process vessels, the disposal method of filter cakes, and the discarding of "gunk from tanks" during plant shutdown. All of these areas had the potential for long-term release of material with concentrated dioxin deposits.

A recurring plant problem was leakage in pumps and piping. Storage, loading and transport leakage would also have resulted in discharges to ground areas. In his deposition, Chonoles reported leaking as the probable source of dioxin discharge from the process into the environment. While there is little quantifiable data supporting this assertion, reports of leakage in units such as the TCP intermediate storage tank and the T reslurry tank as well as possible discharges from storage, transport, and loading operations indicate that leakage was indeed a major source of release of dioxin-containing material into the environment.

In summary, estimated quantities of dioxin released, based on particular discharges that have been documented, fall short of the 96.2 pounds reported by I.T. This assessment suggests that the greater portion of the dioxin contained in site soils would have resulted from discharges associated with day-to-day activities, especially in light of the information provided in depositions and operating reports which suggests that leakage and discharges persisted throughout the period of operation of the plant.

APPENDIX

APPENDIX A

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97b Smith deposition p. 88.

98 Kennedy deposition p. 132, p. 206.

99 Kennedy deposition p. 131.

100 Kennedy deposition pp. 146-147.

101 Kennedy deposition p. 134.

102 Kennedy deposition p. 137.

103 Steward deposition p. 71.

104 Guidi deposition pp. 67-68.

105 Chonoles deposition p. 51.

106 Chonoles deposition p. 126.

107 Steward deposition Exhibit 35, "Operating Comments Plant Technical, January 1969."

108 Kennedy deposition pp. 127-129.

109a Steward deposition pp. 273-274.

109b Heisele deposition pp. 113-114.

109c Smith deposition p. 27-28.

109d Burton deposition p. 307.

109e Burton deposition p. 228.

110 Kennedy deposition p. 325.

111a Kennedy deposition pp. 253-254.

111b Smith deposition pp. 38-39.

111c Smith deposition p. 137.

111d Smith deposition p. 105.

111e Bak deposition pp. 85-87.

112 Kennedy deposition p. 255.

113 Steward deposition p. 271.

114a Chonoles deposition pp. 54-57.

114b Bak deposition p. 85.

115a Guidi deposition p. 168.

115b Smith deposition pp. 35-36.

116 Steward deposition pp. 194-195.

117a Guidi deposition p. 47.

117b Bak deposition p. 63.

117c Heisele deposition p. 98.

118 Guidi deposition p. 174.

119 Kennedy deposition p. 228.

120a Steward deposition p. 51.

120b Burton deposition p. 384.

121a Burton deposition pp. 165-166.

121b Smith deposition p. 32.

121c Bak deposition pp. 132-133.

121d Burton deposition pp. 377-380.

122 Burton deposition pp. 140-141.

123 Kennedy deposition p. 26.

124 Guidi deposition, Volume II p. 75.

125 Steward deposition p. 62.

126 Steward deposition Exhibit 45, "Agriculture Chemicals Division - Newark Plant Operating Comments, December 1969."

127a Letter from Richard Dewling (EPA) to NJDEP Commissioner Hughey, 1983, document number 001460 of the Defense Steering Commitee NJDEP Discovery Documents File.

127b Smith deposition pp. 112-114.

128 Steward deposition p. 89.

129a Burton deposition pp. 73-76.

129b Heisele deposition p. 56.

129c Heisele deposition pp. 115-116.

129d Smith deposition pp. 19-20.

129e Burton deposition p. 294.

129f Bak deposition p. 34.

130 "Dioxins," M.P. Esposito et al, U.S. Environmental Protection Agency, November 1980, EPA-600/2-80-197, p. 247.

131a Burton deposition pp. 167-168.

131b Burton deposition p. 265-266.

131c Smith deposition p. 62.

131d Burton deposition p. 246.

131e Smith deposition pp. 63-64.

131f Smith deposition p. 76-77.

131g Burton deposition p. 302.

131h Burton deposition p. 377-380.

131i Burton deposition pp. 396-397.

131j Smith deposition pp. 95-98.

132 Burton deposition p. 132.

133a Burton deposition pp. 166-167.

133b Smith deposition pp. 50-51.

133c Smith deposition pp. 51-52.

133d Heisele deposition pp. 84-85.

133e Smith deposition p. 55.

134 Steward deposition Exhibits 9-41, "Operating Comments, Plant Technical," November 1966 - July 1969.