

SITE VISIT REPORT

REICHHOLD CHEMICALS, INCORPORATED  
Tacoma, Washington

DATES OF VISIT:  
December 12-16, 1983

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**PURPOSE OF VISIT:**

To identify and microfilm personnel, medical, and workers' compensation records for persons employed in the production of pentachlorophenol. To discuss details of the manufacture of pentachlorophenol and to conduct an industrial hygiene survey of the pentachlorophenol production facility.

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2865 - Industrial Organic Chemicals

## ABSTRACT

A site visit was conducted at Reichhold Chemicals Incorporated, in Tacoma, Washington from December 12-16, 1983. PCP has been shown to be contaminated with polychlorinated dibenzo-p-dioxins and dibenzofurans. Pentachlorophenol production at the Tacoma plant began in 1957 and continued through the period of the site visit. It was determined during this visit that pentachlorophenol workers and maintenance personnel are suitable for inclusion in the Dioxin Registry.

The report includes a description of the review and microfilming of the personnel, medical, and workers' compensation records for those persons who worked in the pentachlorophenol production process. The report also includes a description of the pentachlorophenol process, a summary of analyses of the pentachlorophenol product for hexa-, hepta-, and octachlorodibenzo(p)dioxins, and the results of the industrial hygiene survey conducted by the NIOSH Industrial Hygienist during the site visit.

## INTRODUCTION

The Dioxin Registry defines a cohort of workers who are identified by company records as having worked in the production of chemicals with a known potential for polychlorinated dibenzo(p)dioxin contamination. Because production of these chemicals is not labor-intensive, all U.S. production sites with adequate personnel records are included in the Registry.

Reichhold Chemicals, Incorporated, produces pentachlorophenol (PCP) which has a known potential for contamination by hexachlorodibenzo(p)dioxin (HxCDD), heptachlorodibenzo(p)dioxin (HpCDD) and octachlorodibenzo(p)dioxin (OCDD).

Technical grade PCP, which is known to be contaminated with chlorinated dibenzo-p-dioxins and dibenzofurans, has been shown to cause adverse effects in rat livers.<sup>1,2</sup> Irritation of the eyes and upper respiratory tract, sneezing, coughing, weakness, anorexia, weight loss, sweating, headaches, dizziness, nausea, vomiting, dyspnea, chest pains, and dermatitis have been seen in humans exposed to technical grade PCP.<sup>3</sup> A good overview of the toxicity and health effects of pentachlorophenol can be found in an article by Williams.<sup>4</sup>

From December 12-16, 1983, NIOSH personnel conducted a site visit at Reichhold Chemicals Incorporated in Tacoma, Washington. Personnel, payroll, medical, and workers' compensation records were reviewed and microfilmed. In addition, an industrial hygiene survey was conducted during two shifts to assess the current level of exposures of the workers associated with the PCP production process.

## HISTORY OF PLANT

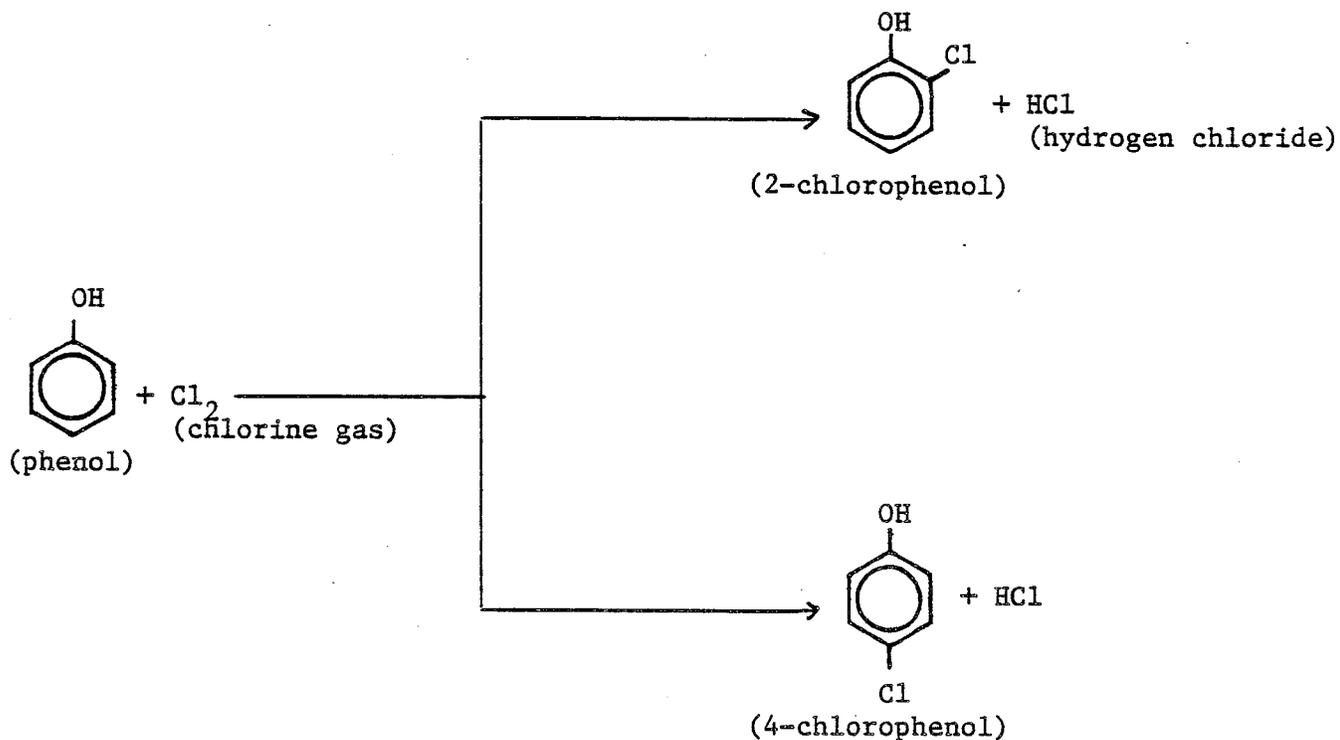
Reichhold Chemicals, Incorporated operated a PCP pilot plant in Seattle, Washington in 1957. Full scale production was begun with the opening of the Tacoma facility in 1958. PCP production still continues at the Tacoma facility. Table 1 lists other products made at or near the PCP production process and the years during which they were produced.

## DESCRIPTION OF THE PENTACHLOROPHENOL PRODUCTION PROCESS

Reichhold Chemicals, Incorporated has produced PCP from 1957 through the time of this site visit. There are three reactors, with two of the reactors in operation since 1958 and third reactor in operation since 1979. The reactor added in 1979 has a larger production capacity and is computer controlled. The basic method for the production of PCP is the same for all three reactors.

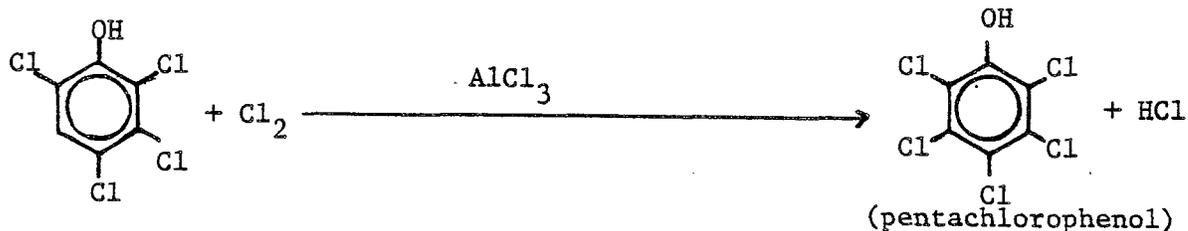
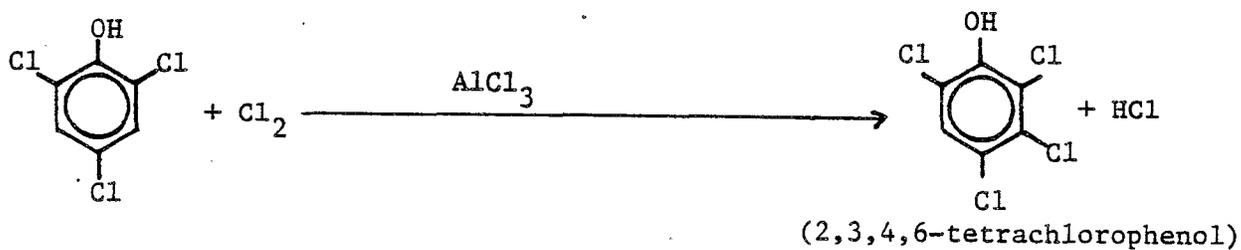
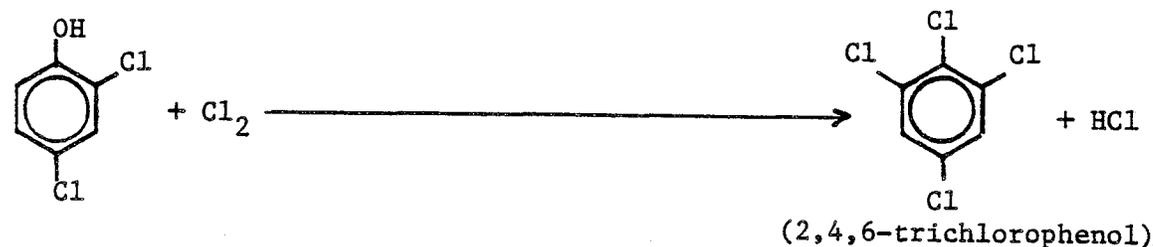
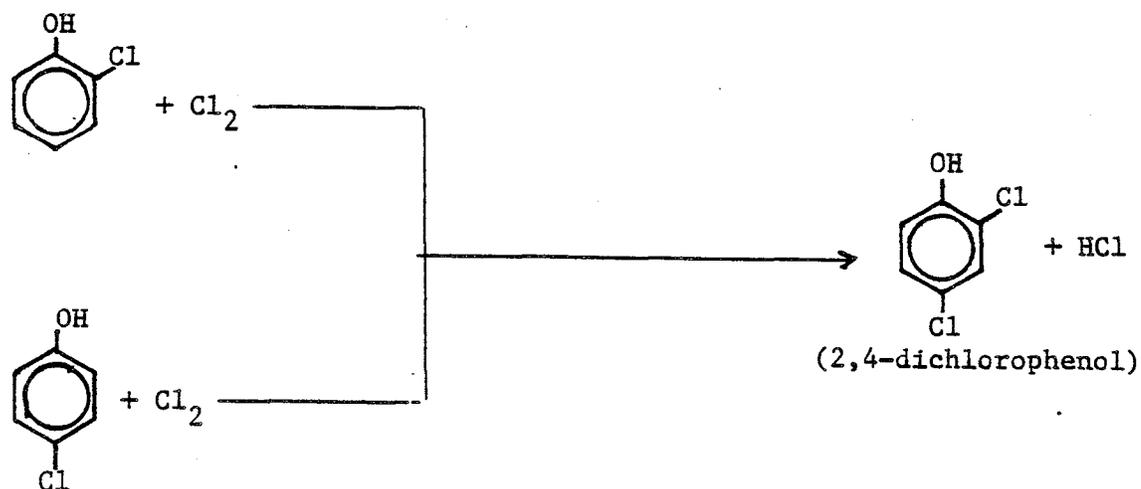
The production of PCP uses the following raw materials: phenol, chlorine gas ( $Cl_2$ ) and anhydrous aluminum chloride catalyst ( $AlCl_3$ ). The PCP production process is best described as two-stage direct chlorination of phenol. A flow diagram for the PCP production process is shown in Figure 1.

The first step in the process takes place in the scrubber. Phenol is pumped to the scrubber storage and from the scrubber storage to the scrubber. The phenol is contacted counter-currently with hydrogen chloride gas containing unreacted chlorine gas which has come from the reactor. The phenol reacts with the chlorine gas as follows:



This reaction takes place in the temperature range between 35° and 55°C. Some dichlorophenols are also formed but the mixture is predominately monochlorophenols. From the scrubber the partially chlorinated phenols are pumped back to the scrubber storage.

The next step in the process takes place in the reactor, a closed jacketed agitated vessel. A portion of the partially chlorinated phenols in the scrubber storage are pumped to the reactor. Anhydrous aluminum chloride catalyst is added to the reactor and chlorine gas is sparged into the reactor contents. The following sequence of exothermic reactions take place:



During this reaction sequence the reactor is maintained between the temperature range of 100° and 120°C until the contents in the reactor reach the tetrachlorophenol stage in the reaction sequence. The various stages in the reactor are monitored by a specific gravity monitor with its readout located in the control room. This temperature range is maintained by applying heat to the reactor jacket and by decreasing and increasing the chlorine gas sparging, which is determined by the generation of hydrogen chloride gas also monitored in the control room. As the reactor contents

approach the PCP stage in the reaction sequence, the temperature is allowed to rise above 120°C. The chlorination continues until the temperature range reaches between 180° and 190°C. During the last hour of the reaction, samples are drawn from the top of the reactor for freeze point determination. The reaction is determined to be complete when a specified freeze point is obtained. Usually four samples are drawn during the freeze point determination. This reaction sequence takes approximately fourteen hours for a full batch in reactors #1 and #2 and 24 hours for a full batch in reactor #3, the computer controlled reactor. For a given batch there is a concentration of 90-92% PCP, 1% tetrachlorophenol and the remainder of the batch is polymers of chlorinated phenols and tars.

Once the reaction to form PCP is complete, the contents in the reactor are pumped to vessels called shot pots. The shot pot vessels are closed jacketed vessels that keep the PCP in a molten state. The PCP is now ready for finishing operations.

PCP is finished in two different methods; either it is prilled or it is molded into blocks. In the prilling operation, the molten PCP is pumped from the shot pots to the top of the prill tower. At the top of the prill tower the PCP is sprayed through a nozzle into a fine mist. Air is blown from the bottom of the prill tower upward, suspending the PCP particles until they amass enough weight to fall to the bottom of the prill tower. At the bottom of the prill tower there is a large shaker screen. The shaker screen filters the prilled PCP and removes the oversized PCP from the bulk of the PCP. From the large shaker screen the prilled PCP is transferred with a long screw auger to a small screen shaker. The small screen removes any oversized PCP particles which were not filtered out by the large shaker screen. The prilled PCP is then transferred from the small shaker screen to the bulk prill storage tank by a closed conveyor called the main elevator. The oversized PCP removed from the prilled PCP is removed from the large and small shaker screens and drummed to be sold as bulk PCP.

From the bulk prill storage tank the prilled PCP is transferred to the bag hopper by a closed conveyor called the bulk elevator. From the bag hopper the prilled PCP is transferred to a pneumatic bagging machine by a closed conveyor called the bagger elevator. The pneumatic bagging machine then automatically fills bags, boxes or drums with prilled PCP to a desired weight. The prilled PCP is now ready for sale.

The other method of finishing PCP is by molding PCP into blocks. The molten PCP in the shot pots is pumped to the molding station where it is poured into large metal molds which form one ton blocks of PCP. The blocks are allowed to cool for approximately three days and then are removed from the molds and wrapped in plastic ready for sale.

At the small shaker screen, the bagger and the molding stations there is a PCP fumes and dust collection system. The PCP fumes and dust from these three sources are vented to a mold bag filter system which filters out the PCP fumes and dust by a bag filter and shakes the collected material from the filter into drums. The drums containing the waste material are then disposed of at a hazardous waste area.

Hydrogen chloride gas is generated as a by-product in the formation of PCP. The hydrogen chloride gas, with unreacted chlorine gas, is vented through pipes from the reactor to the scrubber. In the scrubber the unreacted chlorine gas and any phenols or chlorinated phenols that might have been boiled off are scrubbed from the hydrogen chloride gas.

From the scrubber the hydrogen chloride gas is routed through pipes to the HCl cooler where the hydrogen chloride gas is cooled down and any remaining phenols or chlorinated phenols are condensed and recovered. The cooled down hydrogen chloride gas is then pumped from the HCl cooler to the HCl falling film absorber where the hydrogen chloride gas is absorbed by water to produce 20° Baume hydrochloric acid. The hydrochloric acid is then pumped to a carbon bed which removes organic contaminants which may be present in the hydrochloric acid. From the carbon bed the hydrochloric acid, which is ready for sale, is pumped to a hydrochloric acid storage tank and subsequently put into rail cars and tank trucks.

#### Supplemental Process Information

As noted in the previous section, reactor #3 is computer controlled. Although there is no difference in the basic method of producing PCP in reactor #3 as compared to reactors #1 and #2 there is less direct worker involvement with reactor #3. For example, the computer controls the loading of the reactor with chlorinated phenol feed, thereby eliminating the need for the worker to manually measure the level of raw materials in the reactor. Other safety benefits include alarming on low chlorine vaporizer temperatures, monitoring of product handling systems to prevent spills, and continuous monitoring of process variables to enable immediate response to process deviations.

Reichhold also produces tetrachlorophenol, beginning in the early 1960's and continuing to the present. The process for producing tetrachlorophenol is the same as that used to produce PCP, and the same equipment and raw materials are used. The differences between PCP production and that of tetrachlorophenol are that for the production of tetrachlorophenol the reaction time is shorter, the freeze point needed to determine the end of the reaction is at a lower temperature and the tetrachlorophenol product is flaked instead of being prilled like the PCP. Once a batch of tetrachlorophenol has been produced it is pumped to the tetra shot pot from which it is transferred to a pan in a flaker. A water cooled rotating drum rotates through the molten tetrachlorophenol in the flaker pan. The tetrachlorophenol solidifies on the surface of the drum. As the drum continues to rotate, the solidified tetrachlorophenol is scraped off the surface of the drum into flakes which fall into the bag hopper. From the bag hopper the tetrachlorophenol flakes are bagged, boxed, or drummed in the same manner as the prilled PCP. In the flaker there is a dust and fume collector which collects and routes the tetrachlorophenol dust and fumes to the mold bag filter system. The dust and fumes collected are disposed of in the same manner as the PCP dust and fumes.

Reichhold also produced the sodium salt of PCP, but this was only for a short period of time during the 1960's.

The prilling tower was added to the PCP production process in 1961. Before this time the PCP was flaked in the same manner as the tetrachlorophenol.

#### DESCRIPTION OF THE WORKFORCE

The PCP production process operates for 3 eight hour shifts per day, seven days per week. On the first (day) shift there are five workers involved in the production process, two chief penta operators and three penta operators. On the second (swing) shift and the third (graveyard) shift there are four workers involved in the production process, one chief penta operator and three operators. Table 2 list the duties of these operators.

The chief penta operator spends most of his time in the control room, however his highest potential for routine exposure to hexa-, hepta-, and octachlorodibenzo(p)dioxins occurs when collecting samples for freeze point determination from the reactor towards the end of a batch run. The duties of flaking tetrachlorophenol, bagging PCP, the pouring and pulling of molds of PCP and tetrachlorophenol, changing the shot nozzle in the prilling tower and cleaning the bagging and molding area represent the highest potential routine exposure to hexa-, hepta-, and octachlorodibenzo(p)dioxins for the penta operators. The penta operators also have potential sporadic exposure to hexa-, hepta-, and octachlorodibenzo(p)dioxins when they clean out the mold bag filter system.

Reichhold's Tacoma Washington manufacturing plant routinely has eight members on it maintenance crew. This crew is assigned around the plant with no single member is assigned solely to the PCP product process. Approximately 50% of the total person hours of the maintenance crew are spent in the PCP production process. The most frequent job is repairing leaks in the glass transfer lines at the joints. The maintenance men enter the bag filter house about once every six months to change the filters.

#### PAST EXPOSURE MEASUREMENTS IN THE PENTACHLOROPHENOL PRODUCTION PROCESS

##### Industrial Hygiene Sampling

Reichhold's Tacoma, Washington plant has had four industrial hygiene surveys conducted in conjunction with their PCP production process. Table 3, Results of Past Personal and Area Air Samples for Pentachlorophenol and Tetrachlorophenol, lists the results of these surveys.

The first IH survey was conducted in 1977 by the Hartford Group for Reichhold. The PCP samples were collected by using Millipore matched weight cellulose ester filters and were analyzed by gravimetric techniques. The results of this survey were time weighted average (TWA) PCP concentrations of 34.433 and 7.400 milligrams per cubic meter ( $\text{mg}/\text{M}^3$ ) for the penta operators. The results were reported as  $\text{mg}/\text{M}^3$  of pentachlorophenol, but in actuality these samples were total particulate samples with pentachlorophenol as a component of the total particulate.

The second IH survey was conducted in 1980 by the State of Washington Department of Labor and Industries. The results of this survey were TWA PCP concentrations of 0.0009 mg/M<sup>3</sup> for two penta operators. Other than the results, no other information about the survey is known by NIOSH researchers.

The third and fourth IH surveys were conducted in 1981 and 1983 respectively by Reichhold industrial hygienists. Limited information was made available for the 1981 survey. Three personal samples for PCP for penta operators were collected with the values of 0.33, 0.05 and 0.14 mg/M<sup>3</sup> reported. The sampling for the 1983 survey was conducted by using silica gel sampling media analysed by gas chromatography - electron capture technique. The results of this survey were two TWA PCP concentration results for the chief penta operators of 0.030 and 0.019 mg/M<sup>3</sup> and four TWA PCP concentration results for the penta operators of 0.080, 0.016, 0.008, and 0.023 mg/M<sup>3</sup>.

#### Product and Process Stream Analysis for Polychlorinated Dibenzo(p)dioxins and Other Contaminants Found in Pentachlorophenol

Beginning in December 1981 Reichhold has had samples of the PCP product analyzed for hexachlorodibenzo(p)dioxin (HxCDD), heptachlorodibenzo(p)dioxin (HpCDD) and octachlorodibenzo(p)dioxin (OCDD). A summary of the analytical results are listed in Table 4. The overall mean concentration results for HxCDD, HpCDD, and OCDD in PCP are 10.1 (11.1), 249.0 (209.0), and 1399.6 (1399.6) part per million (ppm) with numbers in parenthesis being the standard deviations. The analysis of the sample for the polychlorinated dibenzo(p)dioxins was performed by HPLC.

Reichhold also had a composite technical grade PCP sample analyzed by California Analytical Laboratory in Sacramento, California for chlorinated dibenzo(p)dioxins dibenzofurans, diphenylethers, "predioxins" and benzenes. Table 5 list the results of this analysis. The results of this analysis showed HxCDD, HpCDD and OCDD concentration levels as being 110, 454 and 800 ppm. This sample was analyzed by gas chromatograph-mass spectrometer. A company official made the following statement about the results listed in Table 5, "The levels of hexachlorodibenzo-p-dioxins and hexachlorodibenzofurans reported are unusually high. There is a significant possibility of interferences, particularly with the polychlorodibenzofurans by polychlorinated diphenyl ethers."

#### DESCRIPTION AND USE OF RECORD SYSTEMS

##### Description of Personnel and Payroll Records

Personnel files have been maintained for all individuals ever employed at the Tacoma plant. The files include application forms, accident reports, some reports of medical examinations, some promotion and transfer orders, and other miscellaneous items. Files for active and terminated hourly employees are maintained in three file drawers in the Personnel Office, and files for salaried individuals are kept in separate file drawers in the same office. Because promotion and transfer slips were not kept for many individuals, it was not possible to use the personnel records to identify all workers employed in pentachlorophenol production or to construct detailed work histories for employees selected for the Registry study.

The payroll records were examined to determine whether adequate information was maintained to identify workers employed in pentachlorophenol or ascertain complete work history information. The company had initiated a computerized payroll system in 1965, and had preserved all quarterly and/or annual summaries. These summaries identify the Cost Center (department) to which each employee was assigned. With the assistance of company representatives it was determined that this information can be used to identify maintenance workers and pentachlorophenol operators employed between 1965 and the present. However, this system does not permit identification of these individuals by job title, and it does not permit identification of persons employed in pentachlorophenol production prior to 1965.

Personnel files for salaried workers do not specify the department to which they were assigned. Company representatives were able to identify all salaried individuals who have worked in the pentachlorophenol department, but there are no records which specify the time periods during which the individuals worked in that department.

A handwritten logbook and a typewritten list were maintained also by the company, and these permitted identification of all persons employed at the Tacoma facility between 1959 and 1964. However, these sources contain no information on the departments to which the individuals were assigned. A comparison of the names recorded in the logbook as employed in 1960 with the personnel files indicated that the personnel files have been retained for all individuals who worked for the company.

#### Medical Records

Prior to 1973 a physical examination was given to individuals at hire and sporadically thereafter. Semiannual examinations were introduced in 1973, and in 1977 the company initiated a program of annual physicals for all employees in the facility. Since 1980, the Puget Sound Occupational Health Clinic has conducted the tests.

#### Identification of the Pentachlorophenol and Maintenance Workers from Payroll Records

With the assistance of the company, the Cost Centers were identified to which the pentachlorophenol and maintenance workers were assigned. Pentachlorophenol production workers have always been assigned to Cost Center 42. Cost Center 40 identifies formaldehyde production; however, this process is located adjacent to the pentachlorophenol process, and its operators have always worked regularly in the pentachlorophenol operation as well as the formaldehyde process. The company estimated that workers in Cost Centers 40 and 42 spent (on the average) about 97% of their time working in the pentachlorophenol process and 3% in the formaldehyde process. Cost Center 48 identifies two processes paratertiarybutylphenol (PTBC) and orthobenzylparachlorophenol (OBPCP) which were run in the same equipment from 1966 to 1983. When these processes were not operating, the operators worked in pentachlorophenol production. The company estimated that workers assigned to Cost Center 48 spent (on the average) about 25% of their time in pentachlorophenol production and 75% in OBPCP/PTBP production.

Maintenance workers have always been assigned to Cost Center 25 and have plantwide responsibilities. The company estimates that maintenance workers spend (on the average) about 25% of their time working in the pentachlorophenol department. It is possible to identify all maintenance employees from 1965 to the present time.

#### DESCRIPTION OF INDUSTRIAL HYGIENE SURVEY METHODS

One objective of the site visit to Reichhold's Tacoma facility was to conduct an industrial hygiene survey of the PCP production process. This survey was conducted during the two first shifts on December 13th and 14th. Personal and area air samples were collected and analyzed for PCP and tetrachlorophenol. Bulk samples of PCP product and freeze point samples, taken from reactor #1, were also collected.

Personal breathing zone samples were collected using Gilian® HFS 113UT and SKC® 124U personal sampling pumps calibrated at a sampling rate of 1.0 liter per minute (L/min). The collection media used was a 2 micron pore size Zefluor filter backed up by a 260/520 milligram silica gel tube. The collection media was changed half way through the shift. Personal samples were collected for the chief penta operators, penta operators, maintenance men, and a lab technician.

Area air samples were collected by using Gilian® HFS 113UT and SKC® 124U sampling pumps calibrated at three different samples rates, 1.0 L/min, 1.7 L/min with and without 10 mm nylon cyclones, and 3.5 L/min. The collection media used was Zefluor filters backed up by silica tubes and silica gel tubes alone for sampling rates of 1.0 L/min. Zefluor filters were used with and without cyclones for the sampling flow rate of 1.7 L/min. Zefluor filters were also used when the sampling rate was 3.5 L/min.

Samples were taken at 1.0 L/m with a filter backed up by a silica tube and with just a silica gel tube to see if there was any appreciable difference between the two sampling methods. Samples were taken at 1.7 L/m with and without a cyclone to address what portion of the PCP particulates were respirable. Samples were collected at 3.5 L/m to see if enough particulate could be collect to measure for airborne dioxins.

Bulk samples were also collected from #1 reactor during the industrial hygiene survey. These samples, which are referred to as freeze point samples, are collected towards the end of the chlorination reaction and are used to determine the completeness of the reaction. Bulk samples were also collected of the pentachlorophenol product. These bulk samples were analyzed for their dioxin and dibenzofuran content.

#### EVALUATION CRITERIA

The current exposure criteria for airborne concentrations of PCP are the Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL),<sup>5</sup> and the American Conference of Governmental Industrial Hygienist (ACGIH) recommended threshold limit value (TLV)<sup>6</sup> of 0.5 mg/M<sup>3</sup>

for an eight hour TWA. There are no PELs or recommended TLVs for airborne concentrations of tetrachlorophenol, hexa-, hepta-, or octachlorodibenzo(p)dioxins. Along with the potential airborne exposure to the above mentioned chemicals there is a potential contribution to the overall exposure by cutaneous routes including mucous membranes and eyes, either by airborne or more particularly, by direct contact with the above mentioned substances.

#### RESULTS, ANALYSES AND DISCUSSION OF INDUSTRIAL HYGIENE SAMPLING

Twenty-eight personal breathing zone samples were collected during the two days of sampling. From the twenty-eight samples, fourteen TWA's were calculated. All the personal breathing zone samples were submitted to Southern Research Institute for determination of PCP and tetrachlorophenols. The collected compounds were desorbed from the Zefluour filters and silica-gel tubes with an acetonitrile/acetic acid solution and analyzed by high performance liquid chromatography (HPLC) with ultra-violet (UV) detection. The column and instrument conditions were octadecyl (C<sub>18</sub>), 25 cm x 0.26 cm ID, reverse phase column and a 254 nm fixed wavelength UV detector.

The column flow rate was 1.0 milliliter per minute and a 100 microliter aliquot per each sample was injected into the column. Both 2,3,4,6- and 2,3,5,6-tetrachlorophenols were eluted at the same retention time and could not be separated. Therefore, quantitative results reported for these two analytes reflect the presence of either or both. The limits of detection for 2,3,4,6 and/or 2,3,5,6-tetrachlorophenol, 2,3,4,5-tetrachlorophenol and pentachlorophenol were 0.90 micrograms (ug) per sample, 1.10 ug/sample and 0.44 ug/sample, respectively. The limits of quantitation for 2,3,4,6 and/or 2,3,5,6-tetrachlorophenol, 2,3,4,5-tetrachlorophenol and pentachlorophenol were 2.70 ug/sample, 3.30 ug/sample and 1.32 ug/sample, respectively.

The results of the personal breathing zone samples are listed in Table 6 and summarized in Table 7 with the means and standard deviations reported being arithmetic means and standard deviations. When calculating the TWAs for the various job titles if one sample result in a given sample set was a less than value, then one half of that value was used to calculate the TWA for that sample set.<sup>7,8</sup> The chief penta operators had a mean PCP TWA of 0.04 (0.03) mg/M<sup>3</sup>; the penta operators had a mean PCP TWA of 0.39 (0.63) mg/M<sup>3</sup>; and the maintenance men had a mean PCP TWA of 0.33 (0.32) mg/M<sup>3</sup>. The numbers in the parenthesis are standard deviations for the respective means. In the course of conducting the survey, it was observed that a sample being worn by a maintenance man was intentionally loaded with PCP containing dust, therefore the sample set associated with this maintenance man was not included in the summaries in Table 7.

One of the TWAs, 1.65 mg/m<sup>3</sup>, was associated with a penta operator who was bagging prilled PCP. The penta operators wear 3M Brand 9920 dust, fume and mist respirators during such operations, therefore their actual exposure would be something less than that which was measured. The other TWA, 0.68 mg/M<sup>3</sup>, was for a maintenance man. No safety equipment was used by this worker.

Eighteen area samples were collected throughout various sites of the PCP process. The same analytical techniques were used to analyze the area air samples as those used to analyze the personal breathing zone samples. The analyses were also for the same analytes. The results of these analyses are listed in Table 8. The PCP TWA area air sample results ranged from 0.005 mg/M<sup>3</sup> (near mold bag filter system) to 0.058 mg/M<sup>3</sup> (near PCP bagging operation). Area air samples were also collected to field test various sample media. The comparison results for these area air samples are listed in Table 9. The comparison of sampling for PCP and TetCP with Zefluour filter backed up by a silica gel tube as compared to only a silica gel tube showed little difference between the two sample media. The comparison of sampling for PCP and TetCP with and without a cyclone showed a significant amount of the PCP and TetCP was non-respirable particularly in the bagging operation area.

Five bulk samples were collected. Two of the bulk samples were freeze point samples taken from reactor #1. Freeze point samples are routinely collected by the chief penta operator towards the end of the chlorination of phenol to determine the completeness of the reaction. Three of the bulk samples were collected of prilled PCP, a final product. The bulk samples were analyzed for di- and tri-, tetra-, penta-, hexa-, and octachlorodibenzo-p-dioxins and octachlorodibenzofuran. The dioxin and furan contaminants were isolated using a two-step isolation procedure using alumina. Quantitation of the dioxins and furans was achieved by using HPLC with a UV detector. Two columns in series; octadecyl (C<sub>18</sub>), 25 cm x 0.26 mm ID each, reversed-phase was used to perform the separation of the various dioxins and furans. The mobile phase was 50% methanol and 50% acetonitrile. The flow rate program was 0.6 mL/min for 10 min and 1.4 mL/min for 35 min. The UV detector was a fixed wavelength of 254 nm and the injection volume was a 20 uL aliquot. The results of the analyses are listed in Table 10. The mean HxCDD and OCDD concentrations in prilled PCP were 14.6 (1.2) ug/g and 377 (72.1) ug/g, respectively (numbers in parenthesis are standard deviations). The mean HxCDD and OCDD concentration in freeze point PCP samples were 14.8 and 175 ug/g, respectively. From these limited sample results it appears there is no significant difference in the levels of HxCDD found in the freeze point samples compared to the prilled PCP. For OCDD measurements it appears there is an appreciable difference between the levels found in the freeze point samples as compared to the prilled PCP samples.

It was not possible to measure dioxins in either the personal breathing zone or area air samples, therefore an estimate based on Reichhold's and the industrial hygiene analytical data on dioxin measurements in PCP was done. Weighted mean values of 10.2 ppm for hexa-, 237 ppm for hepta-, and 1724 ppm for octachlorodibenzo(p)dioxin and 6.4 ppm for octachlorodibenzofuran were calculated from these analytical data. Due to dioxins' low vapor pressure (2,3,7,8-tetrachlorodibenzo(p)dioxin vapor pressure =  $1.7 \times 10^{-6}$  mmHg at 25°C<sup>6</sup>) it is assumed that any airborne dioxins and furans would be associated with particulates and therefore would be collected on the filter portion of the sample media. Using the concentrations of PCP measured on the filter portion of the personal breathing zone samples, estimates were calculated for the dioxins and furans using the weighted means for the

various isomer groups. The results of this exercise are listed on Table 11. It should be emphasized that the results in Table 11 are estimates and not actual measurements. Table 12 summarizes, by job title, the results in Table 11.

### CONCLUSIONS

Hourly employees of Reichhold Chemicals, Incorporated who worked in pentachlorophenol production process and in the maintenance crew are suitable for inclusion in the NIOSH Dioxin Registry. The use of payroll records permits identification of all individuals employed between 1965 and 1983. However, because this system of identification must be used, it is not possible to identify all of the hourly workers who were employed in this process between 1958 and 1964. Therefore workers employed in pentachlorophenol or maintenance only before 1965 will not be included in the study. There are no records which specify the time periods during which salaried employees worked in the pentachlorophenol department; therefore, salaried personnel will not be included. Based on the review of the PCP production process, the analytical data for analysis of hexa-, hepta-, and octachlorodibenzo(p)dioxins in PCP, the industrial hygiene measurements for the PCP process, and the job descriptions, it will be possible to construct an exposure matrix for the PCP workers and the maintenance crew.

### RECOMMENDATIONS

As mentioned in the discussion there were two personal breathing zone TWAs which were above the PEL for pentachlorophenol. While it was noted that the penta operators wore respirators during operations where potential exposure to pentachlorophenol was high, some consideration should be given to lowering this potential exposure, particularly since airborne measurements do not fully address cutaneous routes of exposure. Considerable amounts of dust was observed in the PCP bagging operation. Efforts should be made to reduce the dust generated when bagging PCP. The dust that does enter the work environment should be vacuumed up, not swept up. In the case of the maintenance men, these workers should be required to follow the same safety procedures as those followed by the penta operators when working in the PCP process area.

## REFERENCES

1. Goldstein, J.A., M. Friesen, R.E. Linder, P. Hickman, J.R. Hass and H. Bergman: Effect of Pentachlorophenol on Hepatic Drug-metabolizing Enzymes and Porphyrins Related to Contamination with Dibenzo(p)dioxins and Dibenzofurans. Biochemical Pharmacology, Vol. 26, pp. 1549-1557 (1977).
2. Kimbrough, R.D. and R.E. Linder: The Effects of Technical and Purified Pentachlorophenol on the Rat Liver. Toxicology and Applied Pharmacology, Vol. 46, pp. 151-162 (1978).
3. Baader, E.W. and H.J. Bauer: Industrial Intoxication Due to Pentachlorophenol. Industrial Medicine and Surgery, Vol. 20, pp. 286-290 (1951).
4. Williams, P.L.: Pentachlorophenol, an Assessment of the Occupational Hazard. American Industrial Hygiene Association Journal, Vol. 43, pp. 799-810 (1982).
5. Occupational Safety and Health Administration (OSHA) Safety and Health Standards CFR 1910, General Industrial Standards OSHA 2206, revised June, 1981.
6. Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment with Intended Changes for 1983-84, American Conference of Governmental Industrial Hygienists, 1983.
7. Kushner, E.J.: On Determining the Statistical Parameters for Pollution Concentration from a Truncated Data Set. Atmospheric Environment, Vol. 10, pp. 975-977 (1976).
8. Owen, W.J. and T.A. DeRouen: Estimation of the Mean for Lognormal Data Containing Zeroes and Left-Censored Values, with Applications to the Measurement of Workers Exposure to Air Contaminants. Biometrics, Vol. 36, pp. 707-719 (1980).

TABLE 1

PRODUCTS AND YEARS OF PRODUCTION  
REICHOLD CHEMICALS, INCORPORATED  
TACOMA, WASHINGTON

<u>PRODUCT</u>	<u>YEARS OF PRODUCTION</u>
Pentachlorophenol	1957-1983 Continuous
Formaldehyde	1956-1983 Continuous
Paratertiary Butyl Phenol	1968-1983 (End of Sept.83)
Orthobenzyl Para Chlorophenol	1966-1977 (December)
Hydrochloric Acid	1957-1983 Continuous

TABLE 2

Duties of Pentachlorophenol Operators

Reichhold Chemical, Incorporated  
Tacoma, Washington

A. The Duties of the Chief Operator

- 1) Controls the operation of the process which takes place mostly in the control room.
- 2) Loads aluminum chloride catalyst to the reactor at the beginning of a batch
- 3) Collects samples at the end of a batch for freeze point determination.

B. The Duties of the Operators

- 1) Flakes tetrachlorophenol.
- 2) Bags PCP.
- 3) Pulls molded PCP and tetrachlorophenol.
- 4) Pours PCP and tetrachlorophenol molds.
- 5) Changes shot nozzle in prilling tower.
- 6) Unloads phenol from tank cars.
- 7) Loads hydrochloric acid into tank cars.
- 8) Services and cleans out bag house.
- 9) Transfers hydrochloric acid to the tank farm.

TABLE 3\*

RESULTS OF PAST PERSONAL AND AREA  
AIR SAMPLES FOR PENTACHLOROPHENOL AND TETRACHLOROPHENOL  
REICHOLD CHEMICALS, INCORPORATED  
TACOMA, WASHINGTON

SAMPLE DATE	PERSONAL OR AREA SAMPLE DESCRIPTION	SAMPLE TIME (min.)	PCP CONC. (mg/M <sup>3</sup> )	PCP TWA (mg/M <sup>3</sup> )	TetCP CONC (mg/M <sup>3</sup> )	TetCP TWA (mg/M <sup>3</sup> )	SAMPLING METHOD	ANALYTICAL METHOD
2/9/77	Penta Operator	238	41.447	34.433	-	-	MWF	G
2/9/77	Penta Operator	63	7.936		-		MWF	G
2/9/77	Penta Operator	117	7.173	7.400	-	-	MWF	G
2/9/77	Penta Operator	10	10.00		-		MWF	G
7/1/80	Penta Operator	439	0.0005	0.0009				
7/1/80	Penta Operator	447	0.0009	0.0009				
1/5/81	Penta Operator		0.33					
1/5/81	Penta Operator		0.05					
1/5/81	Penta Operator		0.14					
1/5/81	Base of Shot Tower		0.44					
1/5/81	Control Room		0.10					
1/5/81	Flaker Building		0.36					
4/26/83	Chief Penta Operator	222	0.034		0.030		SiO <sub>2</sub>	GC/EC
4/26/83	Chief Penta Operator	237	0.017	0.025	0.019	0.024	SiO <sub>2</sub>	GC/EC
4/26/83	Penta Operator	229	0.130	0.081	0.080	0.050	SiO <sub>2</sub>	GC/EC
4/26/83	Penta Operator	196	0.023		0.016		SiO <sub>2</sub>	GC/EC
4/26/83	Penta Operator	217	0.009	0.042	0.008	0.016	SiO <sub>2</sub>	GC/EC
4/26/83	Penta Operator	232	0.073		0.023		SiO <sub>2</sub>	GC/EC

\*Table 3 was constructed from documents received from Reichhold

A blank space for a given listing denotes that particular piece of information is not known by NIOSH  
A dash line for a given listing denotes that the particular entry is not applicable for that given entry.

PCP = pentachlorophenol

TetCP = tetrachlorophenol

TWA = time weighted average concentration

MWF = matched weight 0.8 um cellulose ester filters

SiO<sub>2</sub> = silica gel sampling tubes

G = gravimetric techniques

GC/EC = gas chromatography - electron capture techniques

TABLE 4\*

Summary of Polychlorinated Dibenzo(p)dioxin Analysis by HPLC  
in Pentachlorophenol Products

Reichhold Chemical, Incorporated  
Tacoma, Washington

Date	Number of Samples	All Isomers of Hexachlorodibenzo(p)dioxin***				Both Isomers of Heptachlorodibenzo(p)dioxin				Octachlorodibenzo(p)dioxins			
		# of N.D.	Range (ppm)	Mean (ppm)**	Standard Deviation	# of N.D.	Range (ppm)	Mean (ppm)**	Standard Deviation	# of N.D.	Range (ppm)	Mean (ppm)**	Standard Deviation
Dec. 1981	31	12	<0.5-23.2	9.7	8.3	0	139.0-2298.4	286.8	377.3	0	586.8-4883.2	1854.8	851.5
Jan.-Dec. 1982	133	52	<0.5-34.8	11.6	8.6	0	123.0-1794.2	237.5	79.0	0	680.3-9115.0	2135.4	2089.4
Jan.-May 1983	117	63	<0.5-75.6	8.6	12.4	0	36.3-1794.2	222.6	170.8	0	544.4-7537.9	1255.6	1258.0
Total	281	127	<0.5-75.6	10.1	11.1	0	36.3-2298.4	249.0	209.0	0	544.4-9115.0	1399.6	1399.6

\* Table 4 was constructed from documents received from the company.

\*\* When the value was reported as trace it was taken to be less than limit of detection, 0.5 ppm. The means were calculated by using one half of the limit of detection for those samples reported as trace.<sup>5</sup>

\*\*\* There are 10 possible isomers of hexachlorodibenzo(p)dioxin. The analytical techniques used could not differentiate among the different isomers and therefore the results shown are the total hexachlorodibenzo(p)dioxins.

N.D. - Non-detectable Measurements

ppm = parts per million

HPLC = high pressure liquid chromatography

TABLE 5

Neutral Compounds in Pentachlorophenol  
Analysis by California Analytical LaboratoriesReichhold Chemical, Incorporated  
Tacoma, WashingtonPentachlorophenol Composite - Batch #57-, 60-, and 61-2-1078  
October 19, 1978

<u>Compound</u>	<u>Concentration (ug/g)</u>
tetrachlorobenzene	3
pentachlorobenzene	9
hexachlorobenzene	13
hexachlorodibenzo(p)dioxin (all isomers)	110
heptachlorodibenzo(p)dioxin	454
octachlorodibenzo(p)dioxin	800
hexachlorodibenzofuran (all isomers)	887
tetrachlorodiphenylether	35
pentachlorodiphenylether (all isomers)	452
hexachlorodiphenylether (all isomers)	210
heptachlorodiphenylether	300
octachloro "predioxin" (all isomers)	1560
nonachloro "predioxin"	7402

TABLE 6

RESULTS OF PERSONAL BREATHING ZONE SAMPLES FOR PENTACHLOROPHENOL AND TETRACHLOROPHENOL  
 REICHHOLD CHEMICALS, INCORPORATED  
 TACOMA, WASHINGTON  
 DECEMBER 13 and 14, 1983

SAMPLE DATE	PERSONAL AIR SAMPLE DESCRIPTION	FIELD SAMPLE NUMBER RCF&RCT	SAMPLE TIME (min.)	CONC. of PCP on the FILTER (mg/M <sup>3</sup> )	CONC. of PCP in SiO <sub>2</sub> (mg/M <sup>3</sup> )	TOTAL CONC. OF PCP (mg/M <sup>3</sup> )	TWA of PCP (mg/M <sup>3</sup> )	CONC. of TetCP on FILTER (mg/M <sup>3</sup> )	CONC. of TetCP on SiO <sub>2</sub> TUBE (mg/M <sup>3</sup> )	TOTAL CONC of TetCP (mg/M <sup>3</sup> )	TWA of TetCP (mg/M <sup>3</sup> )
12/13/83	Chief Penta Oper.	32	236	0.02	< 0.01	0.02	0.02	< 0.01	< 0.01	< 0.01	< 0.01
12/13/83	Chief Penta Oper.	34	224	0.01	< 0.01	0.01		< 0.01	< 0.01	< 0.01	
12/14/83	Chief Penta Oper.	17	228	0.11	0.02	0.13	0.08	0.67	0.05	0.51	0.27
12/14/83	Chief Penta Oper.	5	250	0.04	< 0.01	0.04		0.09	< 0.01	0.06	
12/14/83	Chief Penta Oper.	8	218	0.03	< 0.01	0.03	0.02	0.10	0.03	0.13	0.07
12/14/83	Chief Penta Oper.	25	265	< 0.01	< 0.01	< 0.01		0.02	< 0.01	0.02	
12/13/83	Penta Operator	33	240	< 0.01	< 0.01	< 0.01	0.07	< 0.01	< 0.01	< 0.01	0.03
12/13/83	Penta Operator	35	220	0.14	< 0.01	0.14		0.05	< 0.01	0.05	
12/13/83	Penta Operator	26	215	< 0.01	< 0.01	< 0.01	0.08	< 0.01	< 0.01	< 0.01	0.05
12/13/83	Penta Operator	19	233	0.16	< 0.01	0.16		0.10	< 0.01	0.10	
12/13/83	Penta Operator	27	215	0.01	< 0.01	0.01	0.02	< 0.01	< 0.01	< 0.01	< 0.01
12/13/83	Penta Operator	40	228	0.01	0.02	0.03		< 0.01	< 0.01	< 0.01	
12/14/83	Penta Operator	12	225	0.18	0.03	0.21	0.15	0.12	0.06	0.18	0.12
12/14/84	Penta Operator	4	240	0.10	< 0.01	0.10		< 0.01	0.06	0.06	
12/14/83	Penta Operator	9	225	0.08	< 0.01	0.08	1.65	0.12	< 0.01	0.12	0.71
12/14/83	Penta Operator	1	238	3.11	0.13	3.14		0.62	0.64	1.26	
12/14/83	Penta Operator	30	222	0.12	< 0.01	0.12	0.37	< 0.01	< 0.01	< 0.01	0.22
12/14/83	Penta Operator	10	238	0.56	0.04	0.60		0.25	0.18	0.43	
12/13/83	Maintenance Man	18	200	1.11	0.36	1.47	0.68	0.09	0.29	0.38	0.26
12/13/83	Maintenance Man	28	286	0.10	0.03	0.13		0.14	0.04	0.18	

TABLE 6 (CONT.)

RESULTS OF PERSONAL BREATHING ZONE SAMPLES FOR PENTACHLOROPHENOL AND TETRACHLOROPHENOL  
 REICHOLD CHEMICALS, INCORPORATED  
 TACOMA, WASHINGTON

SAMPLE DATE	PERSONAL AIR SAMPLE DESCRIPTION	FIELD SAMPLE NUMBER RCF&RCT	SAMPLE TIME (min.)	CONC. of PCP on the FILTER (mg/M)	CONC. of PCP in SiO <sub>2</sub> (mg/M <sup>3</sup> )	TOTAL CONC. OF of PCP (mg/M <sup>3</sup> )	TWA of PCP (mg/M <sup>3</sup> )	CONC. of TetCP on FILTER (mg/M <sup>3</sup> )	CONC. of TetCP on SiO <sub>2</sub> TUBE (mg/M <sup>3</sup> )	TOTAL CONC of TetCP (mg/M <sup>3</sup> )	TWA of TetCP (mg/M <sup>3</sup> )
12/13/83	Maintenance Man	37	200	< 0.01	0.01	0.01	0.05	< 0.01	< 0.01	< 0.01	0.09
12/13/83	Maintenance Man	22	285	0.07	0.01	0.08		0.15	< 0.01	0.15	
12/14/83	Maintenance Man	7+	250	3.00	0.01	3.01	36.06	9.86	0.44	10.30	7.46
12/14/83	Maintenance Man	15+	235	71.16	0.05	71.21		4.34	0.09	4.43	
12/14/83	Maintenance Man	3	250	0.22	0.17	0.39	0.27	0.19	0.22	0.41	0.30
12/14/83	Maintenance Man	2	235	0.13	0.01	0.14		0.18	< 0.01	0.18	
12/14/83	Lab Technician	6	200	0.46	0.06	0.52	0.21	< 0.01	0.03	0.03	0.02
12/14/83	Lab Technician	11	297	< 0.01	< 0.01	< 0.01		< 0.01	< 0.01	< 0.01	

PCP = pentachlorophenol

TetCP = 2,3,4,6-and 2,3,5,6-tetrachlorophenol; samples were also analyzed for 2,3,4,5-tetrachlorophenol but no sample had detectable amounts of this particular isomer

filter: = 2.0 um Zeffluor filter

SiO<sub>2</sub> = 260/520 mg silica gel sampling

TWA = time weighted average concentration

mg/m<sup>3</sup> = milligrams per cubic meter

+ = samples were tampered with

TABLE 7

SUMMARY OF PERSONAL BREATHING ZONE SAMPLES  
 FOR PENTACHLOROPHENOL AND TETRACHLOROPHENOL  
 REICHHOLD CHEMICALS, INCORPORATED  
 TACOMA, WASHINGTON  
 December 13-14, 1983

JOB TITLE	PENTACHLOROPHENOL (mg/M <sup>3</sup> )				TETRACHLOROPHENOL (mg/M <sup>3</sup> )			
	Number of TWA	Range	Mean	Standard Deviation	Number of TWA	Range	Mean	Standard Deviation
Chief Penta Operator	3	0.02-0.08	0.04	0.03	3	< 0.01-0.27	0.12	0.14
Penta Operator	6	0.02-1.65	0.39	0.63	6	< 0.01-0.71	0.19	0.27
Maintenance Man	3	0.05-0.68	0.33	0.32	3	0.09-0.30	0.22	0.11
Lab Technician	1	0.21	-	-	1	0.02	-	-

TWA = time weighted average concentration  
 mg/m<sup>3</sup> = milligrams per cubic meter

TABLE 8

RESULTS OF AREA AIR SAMPLES FOR PENTACHLOROPHENOL AND TETRACHLOROPHENOL  
 REICHHOLD CHEMICALS, INCORPORATED  
 TACOMA, WASHINGTON  
 DECEMBER 13-14, 1983

SAMPLE DATE	AREA AIR SAMPLE DESCR.	FIELD SAMPLE NUMBER RCF&RCT	SAMPLE TIME (min.)	SAMPLE RATE (L/min)	CONC. of PCP on FILTER (mg/M <sup>3</sup> )	CONC. of PCP in SiO <sub>2</sub> (mg/M <sup>3</sup> )	TOTAL CONC. of PCP (mg/M <sup>3</sup> )	TWA of PCP (mg/M <sup>3</sup> )	CONC. of TetCP on FILTER (mg/M <sup>3</sup> )	CONC. of TetCP in SiO <sub>2</sub> TUBE (mg/M <sup>3</sup> )	TOTAL CONC of TetCP (mg/M <sup>3</sup> )	TWA of TetCP (mg/M <sup>3</sup> )
12/13/83	Above Reactor#1	14	238	1.0	0.02	< 0.01	0.02	0.02	0.16	< 0.01	0.16	0.08
12/13/83	Above Reactor#1	29	257	1.0	0.02	< 0.01	0.02		< 0.01	< 0.01	< 0.01	
12/13/83	Above Reactor#1 (SiO <sub>2</sub> tube only)	13	234	1.0	-	< 0.01	< 0.01		-	< 0.01	< 0.01	0.01
12/13/83	Above Reactor#1 (SiO <sub>2</sub> tube only)	23	259	1.0	-	0.02	0.02		-	0.02	0.02	
12/13/83	Above Prilling Tower	39	235	1.0	0.01	< 0.01	0.01	0.01	< 0.01	< 0.01	< 0.01	< 0.01
12/13/83	Above Prilling Tower	24	250	1.0	< 0.01	< 0.01	< 0.01		< 0.01	< 0.01	< 0.01	
12/13/83	Above Prilling Tower (SiO <sub>2</sub> tube only)	RCT 16	234	1.0	-	0.02	0.02	0.01	-	0.06	0.06	0.04
12/13/83	Above Prilling Tower (SiO <sub>2</sub> tube only)	RCT 20	250	1.0	-	< 0.01	< 0.01		-	0.03	0.03	
12/13/83	Above Bagging Operation	38	196	1.0	< 0.01	< 0.01	< 0.01	0.02	< 0.01	< 0.01	< 0.01	0.09
12/13/83	Above Bagging Operation	21	250	1.0	0.04	< 0.01	0.04		0.08	0.07	0.15	

TABLE 8 (CONT.)

RESULTS OF AREA AIR SAMPLES FOR PENTACHLOROPHENOL AND TETRACHLOROPHENOL  
 REICHHOLD CHEMICALS, INCORPORATED  
 TACOMA, WASHINGTON  
 DECEMBER 13-14, 1983

SAMPLE DATE	AREA AIR SAMPLE DESCR.	FIELD SAMPLE NUMBER RCF&RCT	SAMPLE TIME (min.)	SAMPLE RATE (L/min)	CONC. of PCP on FILTER (mg/M <sup>3</sup> )	CONC. of PCP in SiO <sub>2</sub> (mg/M <sup>3</sup> )	TOTAL CONC. of PCP (mg/M <sup>3</sup> )	TWA of PCP (mg/M <sup>3</sup> )	CONC. of TetCP on FILTER (mg/M <sup>3</sup> )	CONC. of TetCP in SiO <sub>2</sub> TUBE (mg/M <sup>3</sup> )	TOTAL CONC of TetCP (mg/M <sup>3</sup> )	TWA of TetCP (mg/M <sup>3</sup> )
12/13/83	Penta Molding Stations	36	198	1.0	0.01	0.01	0.01	0.04	< 0.01	0.05	0.05	0.08
12/13/83	Penta Molding Stations	31	246	1.0	0.03	0.04	0.07		< 0.01	0.10	0.10	
12/14/83	Above Long Screw Auger between large & small shakers (filter only)	42	406	1.7 (cyclone)	0.02	-	0.02	0.02	0.01	-	0.01	0.01
12/14/83	Above Long Screw Auger between large & small shakers (filter only)	16	407	1.7	0.05	-	0.05	0.05	0.07	-	0.07	0.07
12/14/83	Near Mold Bag Filter (filter only)	13	420	3.5	0.005	-	0.005	0.005	0.014	-	0.014	0.014
12/14/83	Near Bagging Oper (filter only).	20	412	1.7	0.058	-	0.058	0.058	0.060	-	0.060	0.060

TABLE 8 (CONT.)

RESULTS OF AREA AIR SAMPLES FOR PENTACHLOROPHENOL AND TETRACHLOROPHENOL  
 REICHHOLD CHEMICALS, INCORPORATED  
 TACOMA, WASHINGTON  
 DECEMBER 13-14, 1983

SAMPLE DATE	AREA AIR SAMPLE DESCR.	FIELD SAMPLE NUMBER RCF&RCT	SAMPLE TIME (min.)	SAMPLE RATE (L/min)	CONC. of PCP on FILTER (mg/M <sup>3</sup> )	CONC. of PCP in SiO <sub>2</sub> (mg/M <sup>3</sup> )	TOTAL CONC. of PCP (mg/M <sup>3</sup> )	TWA of PCP (mg/M <sup>3</sup> )	CONC. of TetCP on FILTER (mg/M <sup>3</sup> )	CONC. of TetCP in SiO <sub>2</sub> TUBE (mg/M <sup>3</sup> )	TOTAL CONC of TetCP (mg/M <sup>3</sup> )	TWA of TetCP (mg/M <sup>3</sup> )
12/14/83	Near Bagging Oper. (filter only)	41	414	1.7 (cyclone)	0.006	-	0.006	0.006	< 0.006	-	< 0.006	< 0.006
12/14/83	Near Bagging Oper. (filter only)	23	402	3.5	0.027	-	0.027	0.027	0.004	-	0.004	0.004

PCP = pentachlorophenol

TetCP = 2,3,4,6- and 2,3,5,6-tetrachlorophenol; samples were also analyzed for 2,3,4,5-tetrachlorophenol but no sample had detectable amounts of this particular isomer

Filter = 2.0 um Zefluor filter

SiO<sub>2</sub> = 260/520 mg silica gel sampling tube

TWA = time weighted average concentration

L/min = liters per minute

mg/m<sup>3</sup> = milligrams per cubic meter

TABLE 9

COMPARISONS OF VARIOUS AREA AIR SAMPLING METHODS  
 REICHHOLD CHEMICALS, INCORPORATED  
 TACOMA, WASHINGTON  
 DECEMBER 13-14, 1983

AREA AIR SAMPLE DESCRIPTION	TYPE OF SAMPLE MEDIA	TWA OF PCP (mg/M <sup>3</sup> )	TWA OF TetCP (mg/M <sup>3</sup> )
Above Reactor #1	filter + tube	0.02	0.08
Above Reactor #1	tube	0.01	0.01
Above Prilling Tower	filter + tube	0.01	< 0.01
Above Prilling Tower	tube	0.01	0.04
Above Long Screw Auger	filter w/o cyclone	0.05	0.07
Above Long Screw Auger	filter w/ cyclone	0.02	0.01
Near Bagging Operation	filter w/o cyclone	0.058	0.06
Near Bagging Operation	filter w/ cyclone	0.006	< 0.006

filter = 2 micron pore size Zefluor filter

tube = 260/520 milligram silica gel

cyclone = 10 millimeter nylon respirable cyclone

TWA = time weighted average

PCP = pentachlorophenol

TetCP = tetrachlorophenol

mg/M<sup>3</sup> = milligrams per cubic meter

TABLE 10

QUANTITATIVE RESULTS FOR ISOMERS OF POLYCHLORINATED DIBENZO(p)DIOXIN AND  
 OCTACHLORODIBENZOZOFURAN IN BULK SAMPLES COLLECTED FROM THE  
 PENTACHLOROPHENOL PROCESS  
 REICHHOLD CHEMICAL, INCORPORATED  
 TACOMA, WASHINGTON

SAMPLE DATE	FIELD NO.	SAMPLE DESCRIPTION	BATCH NO.	CONCENTRATION, ug/g					
				Di&TriCDD	TetCDD	PCDD	HxCDD	OCDD	OCDF
12/14/83	1	Final Freeze Point Sample	21-2-1283	< 1	< 1	< 1	15.1	248	2.99
12/14/83	2	Freeze Point Sample	22-2-1283	5.66	< 1	< 1	14.5	102	< 1
12/14/83	3	Prilled Pentachlorophenol	21-2-1283	< 1	< 1	< 1	13.4	435	3.83
12/14/83	4	Prilled Pentachlorophenol	18-2-1283	< 1	< 1	< 1	15.8	399	6.12
12/14/83	5	Prilled Pentachlorophenol	18-2-1283	< 1	< 1	< 1	14.5	296	9.15

Di&TriCDD = Di- or Trichlorodibenzo(p)dioxin or both (Both di- and trichlorodibenzo(p)dioxin

TetCDD = Tetrachlorodibenzo(p)dioxin

PCDD = Pentachlorodibenzo(p)dioxin

HxCDD = Hexachlorodibenzo(p)dioxin

OCDD = Octachlorodibenzo(p)dioxin

OCDF = Octachlorodibenzofuran

ug/g = micrograms per gram

RESULTS OF ESTIMATED PERSON AIR SAMPLES FOR HxCDD, HpCDD, OCDD and OCDF  
REICHOLD CHEMICAL, INCORPORATED  
TACOMA, WASHINGTON  
DECEMBER 13-14, 1983

SAMPLE DATE	PERSONAL AIR SAMPLE DESCRIPTION	FIELD SAMPLE NUMBER (RCF&RCT)	SAMPLE TIME (min.)	PCP CONC. OF THE FILTER (mg/M <sup>3</sup> )	ESTIMATED DIOXINS AND FURAN EXPOSURES							
					HxCDD CONC. (ng/M <sup>3</sup> )	TWA OF HxCDD (ng/M <sup>3</sup> )	HpCDD CONC. (ng/M <sup>3</sup> )	TWA OF HpCDD (ng/M <sup>3</sup> )	OCDD CONC. (ng/M <sup>3</sup> )	TWA OF OCDD (ng/M <sup>3</sup> )	OCDF CONC. (ng/M <sup>3</sup> )	TWA OF OCDF (ng/M <sup>3</sup> )
12/14/83	Penta Operator	9	225	0.08	0.82	16.7	18.9	388	138	2823	0.51	10.5
12/14/83	Penta Operator	1	238	3.11	31.7		736		5361		19.9	
12/14/83	Penta Operator	30	222	0.12	1.22	3.54	28.4	82.3	207	599	0.77	2.22
12/14/83	Penta Operator	10	238	0.56	5.71		132		965		3.58	
12/13/83	Maintenance Man	18	200	1.11	11.3	5.26	263	122	1913	889	7.10	3.30
12/13/83	Maintenance Man	28	286	0.10	1.02		23.7		172		0.64	
12/13/83	Maintenance Man	37	200	< 0.01	< 0.10	0.44	2.37	10.2	17.2	74.5	< 0.06	0.28
12/13/83	Maintenance Man	22	285	0.07	0.71		16.57		121		0.45	
12/14/83	Maintenance Man	7+	250	3.00	30.6	367	710	8527	5171	62098	19.2	230
12/14/83	Maintenance Man	15+	235	71.2	726		16844		122658		455	
12/14/83	Maintenance Man	3	250	0.22	2.44	1.80	52.1	41.8	379	304	1.41	1.13
12/14/83	Maintenance Man	2	235	0.13	1.33		30.8		224		0.83	
12/14/83	Lab Technician	6	200	0.46	4.69	1.92	109	44.5	793	320	2.94	1.20
12/14/83	Lab Technician	11	297	< 0.01	< 0.10		< 2.37		< 17.2		< 0.06	
12/13/83	Chief Penta Op.	32	236	0.02	0.20	0.15	4.73	3.58	34.5	26.1	0.13	0.10
12/13/83	Chief Penta Op.	34	224	0.01	0.10		2.37		17.2		0.06	
12/14/83	Chief Penta Op.	17	228	0.11	1.12	0.75	26.0	17.4	190	126	0.70	0.47
12/14/83	Chief Penta Op.	5	250	0.04	0.41		9.47		69.0		0.26	
12/14/83	Chief Penta Op.	8	218	0.03	0.31	0.17	7.10	3.85	51.7	28.1	0.19	0.10
12/14/83	Chief Penta Op.	25	265	< 0.01	< 0.10		< 2.37		< 17.2		< 0.06	
12/13/83	Pent Operator	33	240	< 0.01	< 0.10	0.71	< 2.37	16.5	< 17.2	120	< 0.06	0.45
12/13/83	Pent Operator	35	220	0.14	1.43		33.1		241		0.90	
12/13/83	Pent Operator	26	215	< 0.01	< 0.10	0.87	< 2.37	20.3	< 17.2	148	< 0.06	0.54
12/13/83	Pent Operator	19	233	0.16	1.63		37.9		276		1.02	
12/13/83	Pent Operator	27	215	0.01	0.10	0.10	2.37	2.37	17.2	17.2	0.06	0.06
12/13/83	Pent Operator	40	228	0.01	0.10		2.37		17.2		0.06	
12/13/83	Pent Operator	12	225	0.18	1.84	1.42	42.6	32.8	310	239	1.15	0.89
12/13/83	Pent Operator	4	240	0.10	1.02		23.7		172		0.64	

PCP = pentachlorophenol

HxCDD = hexachlorodibenzo(p)dioxin

HpCDD = heptachlorodibenzo(p)dioxin

OCDD = octachlorodibenzo(p)dioxin

OCDF = octachlorodibenzofuran

mg/M<sup>3</sup> = milligrams per cubic meterng/M<sup>3</sup> = nanograms per cubic meter

TWA = time weighted average

+ = sample tampered with

TABLE 12

SUMMARY OF ESTIMATED PERSONAL AIR SAMPLES FOR  
 HxCDD, HpCDD, OCDD, AND OCDF  
 REICHHOLD CHEMICALS, INCORPORATED  
 TACOMA, WASHINGTON  
 DECEMBER 13-14, 1983

JOB TITLE	NUMBER OF TWA	HxCDD (ng/M <sup>3</sup> )			HpCDD (ng/M <sup>3</sup> )			OCDD (ng/M <sup>3</sup> )			OCDF (ng/M <sup>3</sup> )		
		RANGE	MEAN	STANDARD DEVIATION	RANGE	MEAN	STANDARD DEVIATION	RANGE	MEAN	STANDARD DEVIATION	RANGE	MEAN	STANDARD DEVIATION
Chief Penta Operator	3	0.15- 0.75	0.36	0.34	3.58- 17.4	8.28	7.90	26.1- 126	60.1	57.1	0.10- 0.47	0.22	0.21
Penta Operator	6	0.10- 16.7	3.89	6.39	2.37- 388	90.4	148	17.2- 2823	658	1079	0.06- 10.5	2.44	4.02
Maintenance Man	3	0.44- 5.26	2.50	2.48	10.2- 122	58.0	57.6	74.4- 889	422	420	0.28- 3.30	1.57	1.56
Lab Technician	1	1.92	--	--	44.5	--	--	320	--	--	1.20	--	--

HxCDD = hexachlorodibenzo(p)dioxin  
 HpCDD = heptachlorodibenzo(p)dioxin  
 OCDD = octachlorodibenzo(p)dioxin  
 OCDF = octachlorodibenzofuran  
 TWA = time weighted average  
 ng/M<sup>3</sup> = nanograms per cubic meter

Figure 1  
 Pentachlorophenol Production Process Block Flow Diagram  
 Reichold Chemical, Incorporated  
 Tacoma, Washington

