

ESTIMATED WORKER EXPOSURE  
TO 2378 TCDD AND 2378 TCDF  
IN THE MANUFACTURE, PROCESSING, AND  
COMMERCIAL USE OF PULP, PAPER,  
AND PAPER PRODUCTS

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U.S. ENVIRONMENTAL PROTECTION AGENCY  
OFFICE OF TOXIC SUBSTANCES  
401 M STREET, S.W.  
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*by*

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## SECTION 1

### INTRODUCTION

Various isomers of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have been found to be formed during bleaching of wood pulp with chlorine or chlorine-based bleaching chemicals. Quantitative studies conducted by the U.S. Environmental Protection Agency (EPA) and the paper industry (which include the Five-Mill Study, the 104-Mill Study, and the 25-Bleach Line Study) have shown that PCDDs and PCDFs may be retained in low levels in bleached pulp, crude paper products (e.g., unconverted paper, paperboard, fibers), and finished commercial and consumer grade pulp-/paper-based products. Furthermore, PCDDs and PCDFs may also be retained in wastewater and sludge generated during the manufacture of these products or be released to the air through volatilization or particulates.

On July 27, 1988, the EPA entered into a Consent Agreement with the Environmental Defense Fund and National Wildlife Federation regarding a schedule for review of PCDDs and PCDFs from pulp and paper mills. In response to the Consent Decree, EPA is in the process of characterizing risks in order to decide whether to initiate regulatory action to limit PCDD and PCDF production at pulp and paper mills.

The purpose of this report is to aid OTS in its characterization of worker exposure to PCDDs and PCDFs during the manufacturing, processing, and commercial use of pulp, paper, and paper products. A separate report

addresses worker exposure to PCDDs and PCDFs from the processing and commercial use of sludge generated from wastewater treatment operations in paper and pulp mills.

This report is organized into four sections. This section (Section 1) provides the background and purpose of the study. Section 2 provides a profile of industrial processes and operations that may result in exposure to PCDDs and PCDFs during the manufacture of pulp, paper, and paper products. It summarizes the results of the 5-Mill and 104-Mill studies, and includes a workforce characterization for different operations involving the manufacture, processing, and commercial usage of pulp, paper, and paper products. Section 3 discusses the potential for dermal and inhalation exposure to PCDDs and PCDFs for the processes/operations discussed in Section 2. It includes engineering estimates of the levels of inhalation and dermal exposure for workers involved in different types of processes. Section 4 presents the conclusions and recommendations of this study, including a summary of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2378 TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2378 TCDF) daily exposure, toxicity equivalent (TEQ) daily exposure and lifetime average daily exposures, and average and population risks for workers involved in the manufacture, processing, and commercial use of pulp, paper, and paper products. Appendix A presents 2378 TCDD and 2378 TCDF concentrations for bleached pulp on a dry basis, as reported in the 104-mill study. Appendix B presents the methodology employed in this report to calculate average and population risks.

## SECTION 2

### INDUSTRY PROFILE

This section presents descriptions of the operations in pulp, paper-making, and nonwoven fabric production processes that result in formation of and/or worker exposure to PCDDs and PCDFs. It includes results from quantitative studies conducted by the EPA and the paper industry to determine concentrations of PCDDs and PCDFs in streams from pulp and papermaking operations. In addition, the workforce is characterized in detail for those processes with potential for exposure to PCDDs and PCDFs.

#### 2.1 PULP, PAPER, AND NONWOVEN FABRIC MANUFACTURING OPERATIONS

The pulp, paper, and paperboard industry is a major industry in the United States consisting of approximately 700 facilities producing 75 million tons of product annually. It is divided into two major segments: integrated mills where pulp, pulp and paper, or pulp and paperboard are produced; and nonintegrated mills where paper and/or paperboard are manufactured from pulp produced off site. Facilities range from large integrated kraft mills producing over 2000 tons per day to small nonintegrated mills producing less than 1.1 tons per day of product (Hanmer 1988).

The nonwoven industry manufactures many needle punched fabrics from textile (including cellulose) fibers. The fibers are bonded to provide integrity by means of heat bonding (fusion) or a surface application of adhesive. Nonwoven fabric compositions are processed into numerous products

including diapers, sanitary napkins, interliners, medical supplies, and both consumer and work place (medical) garments. Usually nonwoven material which are designed to absorb moisture utilize cellulosic fibers because of their relatively high absorbency. There are approximately 125 plants which use wood pulp to produce nonwovens (Cunningham 1990).

There are three basic pulping techniques currently used in industry: mechanical, semi-chemical, and chemical. Mechanical pulping, which involves separation of wood fibers by mechanical grinding, includes the stone ground-wood refiner, the mechanical and thermomechanical pulping techniques. Semi-chemical pulping, which involves chemical softening of wood chips prior to mechanical grinding, includes the cold-caustic process and neutral sulfite process. Chemical pulping, which involves the chemical separation of wood fibers to dissolve lignin, includes dissolving pulp, sulfite pulp, and kraft pulp techniques (OTA 1989).

The kraft pulping process dominates the pulp and paper industry, accounting for greater than 75 percent of all pulp produced for paper and paperboard in 1987. In addition, the greatest proportion of bleached chemical pulp is produced by the kraft process, which accounts for 88 percent of pulp bleached in 1987 (OTA 1989). There are four significant uses for bleached pulp 1) the manufacture of paper and paperboard either in an integrated or nonintegrated mill, 2) the manufacture of nonwoven textiles, 3) the manufacture of cellulose or cellulose acetate, and 4) the manufacture of powdered  $\alpha$ -cellulose as a food additive. Cellulose is used for producing viscose rayon textile fibers, cellulose di- and tri-acetate textile fibers, and cellulose acetate cigarette filters. The kraft process requires the greatest

degree of bleaching in order to achieve the desired color in the paper products. Mechanical pulping techniques are not studied in this report; mechanical pulp bleaching processes uses bleaching agents other than chlorine such as hydrogen peroxide or sodium hypochlorite (OTA 1989). This report focuses on bleached kraft and sulfite pulp manufacture, the processing of pulp in papermaking and nonwoven fabric production, and the commercial use of these products. This report does not address other uses of pulp in the manufacture of rayon or cellulose acetate for use in textile fibers, filters, and food additives.

Regardless of the pulping technique employed at pulp and/or paper mills, the same general steps are followed in the production of pulp. These include raw material preparation (e.g., debarking and chipping); mechanical and/or chemical separation of wood fibers (i.e., grinding, refining, or digestion) to separate lignin; removal of coloring agents primarily in the form of residual lignin oxidized to a soluble form by bleaching; and either on-site paper formation or drying of pulp into sheets for shipment for off-site paper formation or needle bonding into nonwoven products (OTA 1989). Figure 2-1 shows a flow diagram depicting operations in a typical integrated kraft pulp and paper mill.

#### 2.1.1 Raw Material Preparation

Wood can be received at the pulp mill in several forms. It may be received as short logs of roundwood with bark still attached, as chips, or even as waste sawdust. Typically, roundwood is used and it is debarked by agitating in mechanical strippers or tumbling in steel drums in which wash water may be applied. The debarked wood logs are chipped in a chipper and subsequently are screened, sized, and temporarily stored (OTA 1989). As

# PULP AND PAPER MAKING



Figure 2-1. Typical pulp and paper mill.



dioxin/furan precursors have not yet been exposed to chlorinated compounds, no worker exposure to PCDDs and PCDFs at this stage of the pulp and paper-making process is expected unless PCDD/PCDF is introduced from raw materials or recycled process water.

#### 2.1.2 Fiber Separation

Fiber separation is accomplished in the kraft pulping process by cooking the wood chips in the digester. Chips are fed countercurrently to a fresh chemical stream known as white liquor which contains sodium hydroxide and sodium sulfide. The chips are cooked with steam at 170° to 175°C for a specific time period to separate fibers and to partially dissolve lignin and other extractives (Soklow 1984).

After digestion is complete, the cooked pulp, which is referred to as brown stock, exits the digester into a blow tank. The violent mechanical action separates components of the wood, and steam and volatile materials are separated out of the mixture. The cooked pulp is then sent to the brown stock washing operation that separates cooked pulp from the spent cooking liquor, which is referred to as black liquor. The black liquor is returned to the chemical recovery operations (Soklow 1984).

The most common brown stock washing operation is a three-stage system using rotary filters and countercurrent washing. The suspension of pulp and black liquor is pumped into the first filter where it forms a cake and is washed by effluent from the second filter. The first stage effluent is black liquor which is sent to chemical recovery operations. The cake from the first stage which has been resuspended in the effluent from the second filter is pumped to the second filter. The cake formed in the second filter is washed by effluent from the third filter and is resuspended. It is pumped to

the third filter in which the cake formed is washed with fresh hot water (Soklow 1984).

### 2.1.3 Bleaching Operations

The brown stock must be bleached to produce light colored or white papers preferred for many products, because it still contains an appreciable amount of lignin and other discolorations. Bleaching not only removes and decolorizes lignin but also serves to clean the brown stock of any dirt or foreign matter. Bleaching also removes hemicellulose and extractives (OTA 1989).

Bleaching is normally accomplished in several stages, referred to as multistage bleaching. A typical four-stage bleach plant is presented in Figure 2-2. The bleaching chemicals and the order in which they are used constitute the "bleaching sequence." Bleaching sequences generally contain two phases within each sequence: a delignification segment, whose function is to remove lignin; and a brightening segment, whose principal function is to increase the brightness of the pulp. Delignification segments use chlorination followed by extraction with sodium hydroxide. Brightening segments use sodium hypochlorite and/or chlorine dioxide. Oxygen can be used for the delignification and improved extraction of lignin during the alkali stage (OTA 1989). Table 2-1 presents abbreviations used to designate bleaching sequences.

Several of the most commonly used bleaching sequences in U.S. and Canadian pulp mills are CEDED, CEDH, CEHDED, CEH, and CED. The specific operations of these sequences can be identified by referring to Table 2-1. An

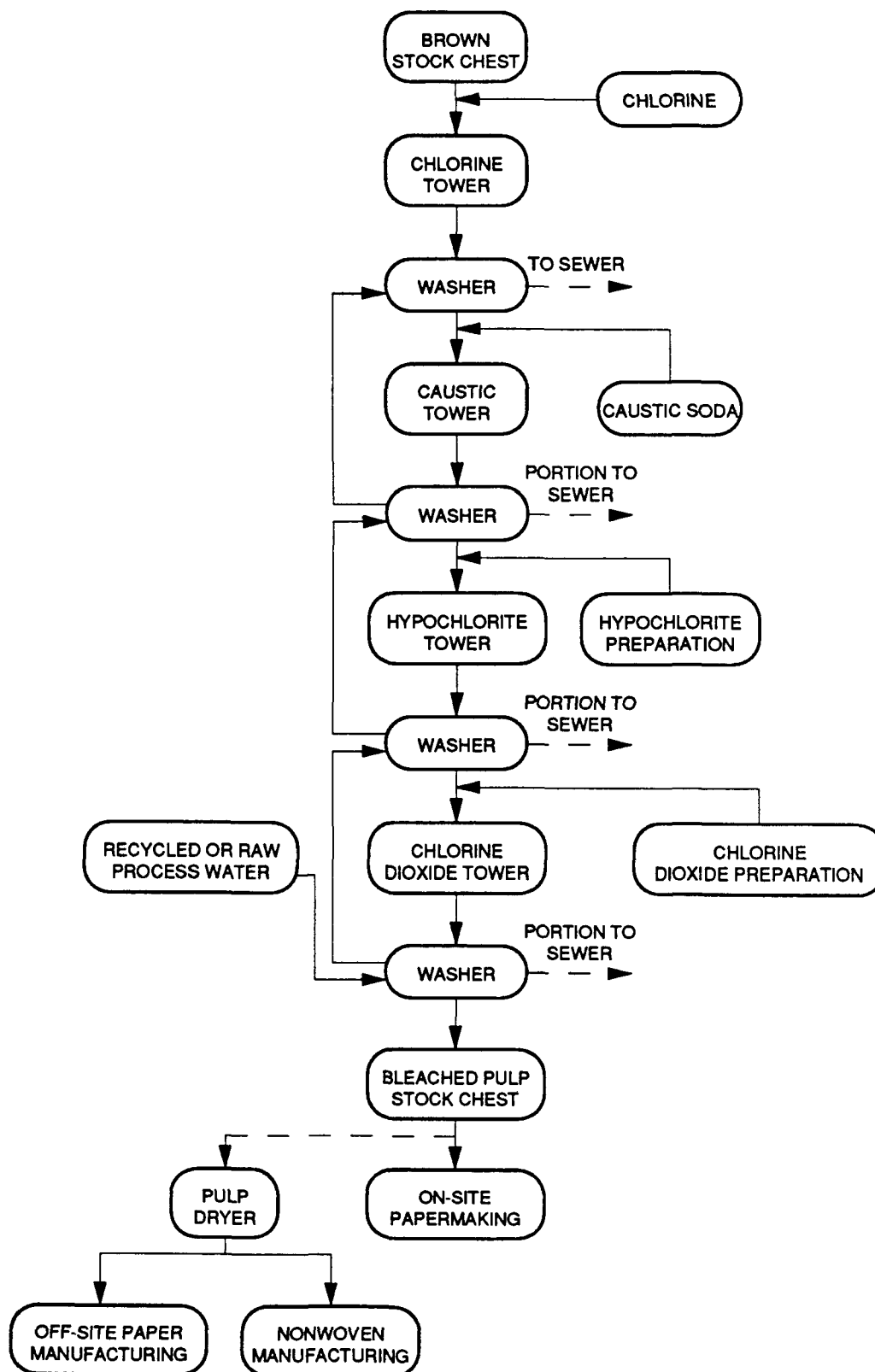


Figure 2-2. Typical four-stage bleach process.<sup>a</sup>

<sup>a</sup> (Soklow 1984 and OTA 1989)

increasing number of mills, however, are currently using oxygen in combination with alkali for extraction ( $E_O$ ) and chlorine dioxide ( $C_D$ ,  $D_C$ ) in the chlorination stage (OTA 1989).

TABLE 2-1. ABBREVIATIONS USED TO DESIGNATE BLEACHING SEQUENCES<sup>a</sup>

| Symbol | Description                      |
|--------|----------------------------------|
| C      | Chlorination                     |
| E      | Extraction with sodium hydroxide |
| H      | Hypochlorite (sodium or calcium) |
| D      | Chlorine dioxide                 |
| P      | Hydrogen peroxide                |
| O      | Oxygen                           |
| N      | Nitrogen dioxide                 |
| Z      | Ozone                            |

<sup>a</sup> OTA 1989.

Note: Two bleaching agents may be used in a single stage. For example, chlorine gas and chlorine dioxide are sometimes combined in an early bleaching stage. If chlorine gas is the predominant agent in the mixture, the treatment would be designated " $C_D$ ." If the chlorine dioxide is the predominant agent in the mixture, the treatment would be designated " $D_C$ ."

In the bleaching process, each stage consists of a closed reaction tower in which the pulp is retained in contact with the particular chemical agent for the optimum retention time. The pulp is washed in vacuum washers or diffusers and then proceeds to the next stage of the bleaching process. (Soklow 1984). The water used for washing is either raw water or white waters recycled from papermaking operations. Typically, the wash water is introduced into the washer associated with the final stage and proceeds by countercurrent flow to washers associated with the previous stage of bleaching. The rinsing operations can be, and often are, open to the atmosphere. After the final stage of bleaching, the bleached pulp is placed in a storage tank, awaiting further processing into a variety of products (OTA 1989).

All process operations used during a particular bleaching sequence constitute the "bleach line." Bleach lines have an average pulp processing rate of 600 tons/day. For the most part, pulp mills have either one or two bleach lines (Hawks 1989).

#### 2.1.4 Pulp Drying

Pulp to be used off site (in paper, nonwovens, textile fibers, filters, food additives, etc.) is usually dried and either formed into sheets or baled before shipment. Pulp drying is achieved by first partially dewatering the pulp on a Fourdrinier or cylinder, pressing it into sheets, and then drying it by contact with heated rotating cylinders or while conveying through a hot-air drying chamber. Some mills in recent years have used flash-drying systems in which the pulp is shredded after being dewatered and pressed, and is then simultaneously conveyed and dried in a hot-air drying system. The last preparation of the pulp before shipment is the final pressing and baling of the pulp. Most drying operations in the industry are automated to some degree. The white waters generated during pulp drying are usually recycled back to the system in certain areas, such as the head box or the debarking equipment (McCubbin 1989).

#### 2.1.5 Papermaking Operations

Papermaking operations occur at integrated mills where both pulp and paper are produced onsite, and at nonintegrated mills where paper is manufactured from pulp produced offsite. Pulp is delivered from the pulp mill to papermaking operations in an aqueous slurry (in the case of integrated facilities), or as dry sheets, referred to as laps, which must be slushed prior to processing (in the case of nonintegrated facilities) (Kirk-Othmer 1981a). In

1987, 86 percent of the sulfite and kraft pulp consumption belonged to integrated mills consuming their own pulp (Census 1988). Figure 2-3 presents a flow diagram for a typical papermaking plant.

Almost all of the pulp is subjected to mechanical action prior to paper sheet formation to improve the strength and other physical properties of the finished sheet. This mechanical action is referred to as beating or refining. Various additives are introduced into the pulp depending upon the desired grade of paper. These include sizing additives, fillers, and coloring agents. The refined pulp, into which the various additives are incorporated, is referred to as furnish (Soklow 1984).

The furnish is further diluted with recycled white water from the papermaking machine to form a mixture containing approximately 0.5 percent fiber (Soklow 1984). The diluted slurry is cleaned in cyclone cleaners and screened in centrifugal screens prior to feeding into the "wet-end" of the papermaking machine (OTA 1989).

The standard papermaking machine in the industry is the Fourdrinier machine. There may be a wide range of papermaking machines used at a particular facility; in general, however, most plants operate two machines (Kirk-Othmer 1981a). The number of machines used at a papermaking facility typically ranges from one to four, with production volumes typically ranging from 200 to 1500 tons per day (Hawks 1989). The diluted slurry passes through the head box of this machine in which the slurry is uniformly distributed over the desired sheet width. A sheet of pulp is formed on the continuously-moving Fourdrinier wire which is a bronze or polymer screen. Water drains from the pump sheet through the screen mesh; increased water removal is facilitated by foils, table rolls, and suction boxes (Soklow 1984).

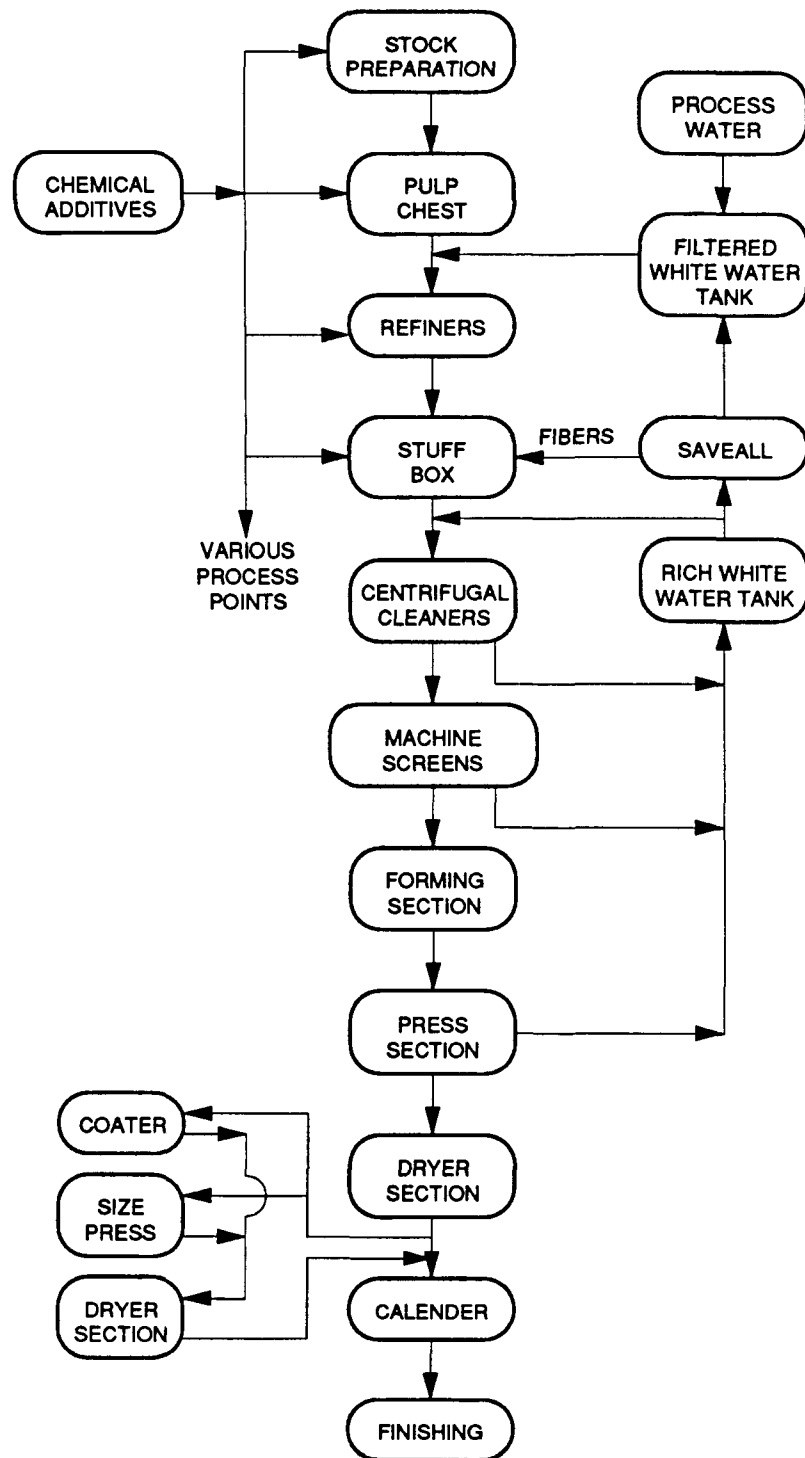


Figure 2-3. Typical closed papermaking process.<sup>a</sup>

<sup>a</sup> (Soklow 1984)

The wet sheet is continuously lifted from the Fourdrinier wire by the couch roll and is transferred to the wet-pressing section. The wet-pressing section is a woven felt belt where additional water is removed by pressure rollers. The paper passes into the drying section where the remaining water is removed by hot air circulated under a hooded ventilation system. After drying, the sheet may pass through a coater (where a combination of pigments, adhesives, and additives are applied) and an additional drying section, prior to pressing through the calendar rolls. Pressing with calendar rolls imparts a surface finish to the paper sheets by a combination of compression and friction. Usually two stacks of calendar rolls are used in paper manufacturing operations. The paper sheets are then wound onto the reel (Soklow 1984). Coating may occur in a separate operation following drying and calendering.

Finishing operations begin after the last operation of the papermaking machine and end where the product leaves the mill. These operations include coating, supercalendering, rewinding, slitting, cutting and sheeting, trimming, packaging, and shipping. Supercalenders are used to impart a smoother finish to the paper. Rewinders are used to reduce the machine width sheets into smaller widths to meet customer specifications and are equipped with slitters which are used to cut paper sheets into specific lengths. Trimmers are used to trim the dimensions of a paper sheet to its final exact size. The last part of the finishing operation involves packaging of the paper-based product and preparing it for shipping (Soklow 1984).

A variety of finishing operations will be employed, depending upon the grade of paper manufactured and the intended end-product use. In addition, the product determines the mix of various types of pulp. For instance, sulfite pulp is used in the manufacture of fine and printing papers; bleached



kraft pulp is used to produce paperboard and tissue, printing, and writing papers; and dissolving kraft or sulfite pulp is used in the manufacture of viscose rayon and acetate fibers (OTA 1989).

#### 2.1.6 Converting Operations

Nearly all paper is converted by undergoing further treatment after manufacture. Among the many converting operations are embossing, impregnating, saturating, laminating, and forming of specific shapes and sizes such as bags and boxes (Kirk-Othmer 1981a). Converting operations may be done at papermaking mills or at facilities which simply purchase paper stock from the papermaking mills. There are thousands of converting establishments which purchase and process paper stock into a wide variety of products. Consequently, it is rather difficult to define a single converting operation which would be representative of the entire converting industry (Festa 1989).

There are very limited data in the open literature on converting operations for bleached kraft paper. Bleached paper and paperboard are used for products such as envelopes, tissue, writing, bond, and publication and printing paper, shipping bags and sacks, linerboard, folding cartons, milk cartons, and paper plates and towels. The operations used to convert paper stock into these products may involve cutting, slitting, and hole punching of the paper stock. These operations may result in the creation of paper dust, and involve manual handling of the paper stock and finished product.

#### 2.1.7 Nonwovens

The nonwoven industry produces goods such as disposable diapers, hospital wear, bandages, medical supplies, sanitary napkins, wipes, towels, and other associated products. Raw materials used for the production of these goods include wood pulp, synthetic and textile fibers, and cellulosic fibers.

Wood pulp makes up only 5 percent of the raw materials used in the nonwoven industry (Nonwovens 1989). In 1988, the nonwoven industry consumed over 100,000 metric tons of bleached pulp that was manufactured (Grant 1990). The most popular pulp converting production techniques include wet formation, thermal bonding, fiber entanglement, and needle-punching. Dried pulp is received in roll form from a pulp mill and is transported by forktruck to the unwinder. The pulp roll is unwound into a pulp sheet and is manually or automatically fed into the hammer mill, which shreds and fluffs the pulp sheet. Typically, pulp dust resulting from the hammer mill is reclaimed through a vacuum screen formed by a vacuum filter. The pulp fluff is then placed on a forming belt and is machined, wrapped, and packaged using various techniques and equipment. The nonwoven industry has an equally varied list of products and manufacturing techniques as paper converting, therefore a general description of the product finishing step could not be defined (Cunningham 1990). Most machines used in the nonwoven industry are highly automated. Operations in the nonwoven industry include spun bonded, spun laced, dry laid, wet laid, melt blown, and melt blown composites. All are not adaptable to cellulosic fibers.

## 2.2 DIOXIN FORMATION IN PULP AND PAPER MILLS

Samples of pulp and paper mill wastewater treatment effluent and sludge, as well as bleached pulp and bleached pulp-based products, have shown that PCDDs and PCDFs are formed during the bleaching of pulp if chlorine or possibly chlorine compounds are used as bleaching agents. Three isomers dominate the PCDD and PCDF formation during chlorine bleaching of chemical pulp (Voss 1988):

2,3,7,8-tetrachlorodibenzo-p-dioxin (2378 TCDD)  
2,3,7,8-tetrachlorodibenzofuran (2378 TCDF)  
1,2,7,8-tetrachlorodibenzofuran (1278 TCDF)

Of the TCDD isomers, only 2378 TCDD was found in detectable quantities in pulp mill wastes. The total of other TCDDs were not detected at a detection level of 1 ppt (Kuehl et al. 1987). The TCDF compounds found in pulp mill wastes were dominated by two isomers, 2378 TCDF and 1278 TCDF, but other TCDF isomers were present in minimal quantities. Previous studies have mainly focused on 2378 TCDD, which is the most toxic member of the PCDD and PCDF family, and 2378 TCDF, which is believed to be one-tenth as toxic as 2378 TCDD.

#### 2.2.1 PCDD and PCDF Precursors and Formation

The chemical reactions and conditions under which PCDDs and PCDFs are formed in pulp and papermaking operations are not yet completely understood. PCDDs and PCDFs are formed as byproducts during these manufacturing operations and are considered contaminants. Chlorination of a PCDD or PCDF precursors in the pulp during bleaching stages may result in the production of chlorinated dioxins, furans, and other chlorinated organic compounds which are of concern to human health.

Possible sources of PCDD and PCDF precursors include natural constituents in wood, contaminants in plant pipes and machinery, and additives (OTA 1989). PCDD/PCDF formation may result from condensation of chlorophenols formed by chlorination of naturally occurring phenolic compounds such as lignin, which comprises 25 percent of wood (Beck 1988). To date, the only substances found to contain precursors that have been studied in depth are the oil-based defoamers, which are additives that enhance the washing of unbleached pulp by controlling foam production.

A recent Canadian study (Voss 1988) has uncovered the possibility that oil-based defoamer additives may be serving as carriers of unchlorinated precursor compounds. The study positively identified the presence of one PCDF precursor, dibenzofuran (DBF), which is a contaminant in oil-based defoamers. The study revealed the potential for DBF contamination in tap water used for process makeup water, air, and raw wood. The presence of another precursor, dibenzo-p-dioxin (DBP), was suspected in oil-based defoamers; however, it could not be confirmed because of excessive interference from other substances during analysis. Tests revealed that the addition of oil-based defoamers resulted in elevated levels of 2378 TCDD and 2378 TCDF in the final chlorinated pulp. The pulp and paper industry is currently investigating replacements for oil-based defoamers, but little information is available on the extent of replacement of oil-based defoamers or the limitations of the substitutes. One contact stated that his company successfully replaced the oil-based defoamers without affecting operations. A NCASI/API joint study is currently being performed as a followup study to the 104-Mill Study. This study will investigate the effectiveness of measures taken by certain mills to reduce PCDDs and PCDFs. The followup study will include the extent of oil-based defoamer replacement and the resulting reduction of PCDD/PCDF production (Grant, 1990). Table 2-2 presents data on the effect of defoamer addition to laboratory-prepared brown stock kraft pulp on subsequent 2378 TCDD and 2378 TCDF formation during the bleaching process. The data were collected from studies using laboratory-prepared western hemlock kraft pulp. Various oil-based defoamers were added at 1 percent the weight of the pulp, which is 10 times greater than normal industry practice. This was done so

that oil-based defoamers could be identified as being the source of the precursors.

TABLE 2-2. EFFECT OF DEFOAMER ADDITION TO BROWNSTOCK KRAFT PULP ON SUBSEQUENT DIOXIN FORMATION DURING THE BLEACHING PROCESS<sup>a</sup>

| Pulp additive                                       | 2378 TCDD concentration, ppt | 2378 TCDF concentration, ppt |
|---|------------------------------|------------------------------|
| None  | 11                           | 160                          |
| 1% of oil-based defoamer A (virgin oil base)        | 110                          | 910                          |
| 1% of oil-based defoamer B from Canadian kraft mill | 81                           | 280                          |
| 1% of oil-based defoamer C (recycled oil base)      | 140                          | 1200                         |
| 1% of recycled oil base used in defoamer C          | 170                          | 1400                         |

<sup>a</sup> Source: (Voss 1988)

#### 2.2.2 Quantitative Studies

In an attempt to quantify concentrations of PCDD and PCDF produced during pulp and paper manufacturing operations, several recent studies have been undertaken by the EPA and the paper industry. These studies include the Cooperative Dioxin Screening Study (or Five-Mill Study), the 104-Mill Study, and the 25 Bleach Line Study. The Five-Mill Study and 104-Mill Study were undertaken as a joint investigation by EPA and the industry, whereas the 25 Bleach Line Study is solely industry-sponsored. Data have been released from the Cooperative Dioxin Screening Study and the 104-Mill Study; however, the results of the 25 Bleach Line Study (which involves measurements of PCDD and PCDF concentrations in effluent, sludge, pulp and intermediate pulps, and filtrates) will not be available until early 1990 (Bond 1989).

All of these studies involve analysis of PCDD and PCDF concentrations from the bleaching of kraft pulp. Kraft pulp was selected for a number of reasons. Sampling data from screening studies conducted by EPA revealed that the highest concentrations of PCDDs and PCDFs within the paper industry were associated with kraft pulp mills (Hanmer 1988). Chlorine and chlorine derivatives, which are necessary for PCDD and PCDF formation, are used in the kraft pulp bleaching process.

#### 2.2.2.1 Cooperative Dioxin Screening Study--

The Cooperative Dioxin Screening Study, or Five-Mill Study, was conducted from June 1986 to January 1987 at five bleached kraft pulp and paper mills as a joint investigation by EPA and the industry. The study focused on three mills known to have PCDD/PCDF in their waste sludge and two additional mills that were volunteered by their firms to provide geographical coverage. In this study, concentrations of 2378 TCDD and 2378 TCDF were measured in unbleached and bleached pulps, bleach line filtrates, paper machine wastewater, sludge, and wastewater effluent. The results of this study indicated that the bleaching of kraft pulp with chlorine and chlorine derivatives is responsible for the production of 2378 TCDD and 2378 TCDF as byproducts of the kraft pulping process.

Table 2-3 presents a summary of the range, mean, and median concentrations for 2378 TCDD toxicity equivalents (TEQ) and the corresponding range of 2378 TCDD and 2378 TCDF concentrations in unbleached and bleached pulp from the five mills. The TEQ values reflect the relative toxicity of 2378 TCDF with respect to 2378 TCDD. Equation 1A is used to calculate TEQ while Equation 1B is used for calculating the percent contribution due to 2378 TCDD.

$$TEQ = C_{TCDD} + 0.1 C_{TCDF} \quad \text{Equation 1A}$$

$$\%TCDD = \frac{C_{TCDD}}{C_{TCDD} + C_{TCDF}} \times 100 \quad \text{Equation 1B}$$

where TEQ = toxicity equivalent, ppt

$C_{TCDD}$  = concentration of 2378 TCDD in pulp, ppt

$C_{TCDF}$  = concentration of 2378 TCDF in pulp, ppt

%TCDD = percent of the contribution due to 2378 TCDD, percent

The low and high plant TEQs provide the lower and upper ranges of 2378 TCDD and 2378 TCDF concentrations.

TABLE 2-3. SUMMARY OF TEQ AND CORRESPONDING 2378 TCDD AND 2378 TCDF CONCENTRATIONS IN UNBLEACHED AND BLEACHED PULPS (FIVE-MILL STUDY)<sup>a</sup>  
(ppt)

| Pulp type               | No. of samples | TEQ                |      |        |                 |                 |
|-------------------------|----------------|--------------------|------|--------|-----------------|-----------------|
|                         |                | Range <sup>b</sup> | Mean | Median | 2378 TCDD range | 2378 TCDF range |
| Unbleached <sup>c</sup> | 8              | 0.17(57)-0.72(18)  | 0.40 | 0.36   | 0.16-0.49       | 0.12-2.3        |
| Bleached <sup>d</sup>   | 9              | 0.56(45) - 69(22)  | 22.2 | 9.6    | 0.5-51          | 0.6-180         |

<sup>a</sup> EPA 1988. Concentrations reported on a dry basis.

<sup>b</sup> Values in parentheses are percent contributions due to 2378 TCDD.

<sup>c</sup> 2378 TCDD was not detected in all samples with detection levels of 0.3 to 1 ppt. 2378 TCDF was not detected in five samples with detection levels of 0.16 to 0.27 ppt.

<sup>d</sup> 2378 TCDD was not detected in two samples with detection levels of 0.62 and 1.0 ppt. 2378 TCDF was not detected in one sample with a detection level of 1.2 ppt.

For the purpose of calculating TEQ range, mean, and median concentrations, PEI assumed the concentration of samples in which 2378 TCDD and 2378 TCDF were not detected to be half of the detection level. It must be noted

that the mean and median concentrations presented in Table 2-3 may not necessarily be representative of all pulp and paper mills.

Although no 2378 TCDD was detected in unbleached pulp, three of the seven samples tested above detection levels for 2378 TCDF. The positive analysis for 2378 TCDF in unbleached pulp may be due to reuse of PCDF and PCDD contaminated paper machine wastewater for brown stock pulping or dilution at the mill where the samples were taken. Most of the bleached pulp samples tested positively for 2378 TCDD and 2378 TCDF, which led to the hypothesis that their formation originated in the kraft bleaching process.

Table 2-4 presents a summary of the range, mean, and median concentrations for the TEQ and corresponding range of 2378 TCDD and 2378 TCDF concentrations in untreated filtrates from the various stages of the bleaching processes used at the five mills. All of the samples tested above detection levels for 2378 TCDF. In five samples, 2378 TCDD was not detected. For the purpose of calculating TEQ range, mean, and median concentrations, PEI assumed the concentration of samples in which 2378 TCDD and 2378 TCDF were not detected to be half of the detection level. It must be noted that the mean and median concentrations presented in Table 2-4 may not necessarily be representative of all pulp and paper mills. The low and high plant TEQs provide the data points for the lower and upper ranges of 2378 TCDD and 2378 TCDF concentrations.

Table 2-4 shows that filtrate wastewater from the caustic extraction stage generally contained the highest concentrations of 2378 TCDD and 2378 TCDF, followed by the hypochlorite, chlorination, and chlorine dioxide stages. The bleach plant filtrate data do not clearly define the point of 2378 TCDD and 2378 TCDF formation but do indicate formation in the chlorination



TABLE 2-4. SUMMARY OF TEQ AND CORRESPONDING 2378 TCDD AND 2378 TCDF CONCENTRATIONS IN FILTRATES FROM VARIOUS STAGES OF THE BLEACHING PROCESS (FIVE-MILL STUDY)<sup>a</sup>  
(ppt)

| Filtrate type                                      | No. of samples | TEQ                       |       |                 |                 |                 |
|--|----------------|---------------------------|-------|-----------------|-----------------|-----------------|
|  |                | Range <sup>b</sup><br>(3) | Mean  | Median          | 2378 TCDD range | 2378 TCDF range |
| C stages<br>(C, C <sub>D</sub> , C/D) <sup>c</sup> | 8              | 0.012(3)-0.62(6)          | 0.14  | 0.059           | 0.003-0.24      | 0.093-3.8       |
| E stages<br>(E, E <sub>0</sub> ) <sup>d</sup>      | 9              | 0.012(10)-5.1             | 1.61  | 0.31            | 0.006-1.8       | 0.056-33        |
| H stages<br>(H, H/D) <sup>e</sup>                  | 10             | 0.019(7)-2.8(17)          | 0.62  | 0.28            | 0.008-1.9       | 0.11-9.2        |
| D stages (D) <sup>f</sup>                          | 2              | 0.0034(13)-0.043(19)      | 0.023 | NA <sup>g</sup> | 0.002-0.03      | 0.014-0.13      |

<sup>a</sup> EPA 1988.

<sup>b</sup> Values in parentheses are percent contributions due to 2378 TCDD.

<sup>c</sup> C Stage represents chlorination stage of the mills. C represents use of chlorine only. C<sub>D</sub> represents use of a mixture of chlorine dioxide and chlorine, which is predominantly chlorine. C/D represents use of a mixture of chlorine and chlorine dioxide. 2378 TCDD was not detected in one sample (C<sub>D</sub>) with a detection level of 0.006 ppt.

<sup>d</sup> E Stage represents caustic extraction stage following the bleaching stages at the mills. E represents use of sodium hydroxide only. E<sub>0</sub> represents use of a mixture of sodium hydroxide and oxygen, which is predominantly sodium hydroxide. 2378 TCDD was not detected in two samples (both E<sub>0</sub>) with detection levels of 0.011 and 0.033 ppt.

<sup>e</sup> H Stage represents hypochlorite stage of the mills. H represents use of sodium or calcium hypochlorite only. H/D represents use of a mixture of sodium or calcium hypochlorite and chlorine dioxide. 2378 TCDD was not detected in one sample (H) with a detection limit of 0.017 ppt.

<sup>f</sup> D stage represents chlorine dioxide stage at the mills. D represents use of chlorine dioxide only. 2378 TCDD was not detected in one sample with a detection level of 0.003 ppt.

<sup>g</sup> NA = Not applicable.

(C) stage and possibly in the extraction (E) stage. It is not possible from the data to determine whether 2378 TCDD and 2378 TCDF are formed in the C stage and extracted in the E stage or if there is additional formation in the E stage. The data also suggest formation of these compounds in subsequent bleaching stages (EPA 1988).

In summary, the results of the Cooperative Dioxin Screening Study indicate that 2378 TCDD and 2378 TCDF are formed during the bleaching of kraft hardwood and softwood pulps with chlorine and chlorine derivatives, and that they are the principal PCDDs and PCDFs found in samples.

At the time of the Five-Mill Study, information regarding the possibility of the presence of PCDD and PCDF precursors in oil-based defoamers was not available. Depending on the extent of use of water-based or other types of defoamers in industry today (and a knowledge of the washing stages in which they are introduced), concentrations of 2378 TCDD and 2378 TCDF found in the Five-Mill Study may therefore be higher than those representative of current industry practices.

#### 2.2.2.2 The 104-Mill Study--

The 104-Mill Study or Cooperative Dioxin Study was conducted from April 1988 to August 1989 at 104 domestic pulp mills manufacturing chemical pulp as a joint investigation by EPA and the industry. In this study, concentrations of 2378 TCDD and 2378 TCDF were measured at 87 kraft (sulfate) and 17 sulfite pulp mills that use chlorine-based bleaching processes (chlorine, chlorine dioxide, or hypochlorite). Samples were taken of the following: 1) bleached pulp after the final stage of bleaching, 2) combined dewatered wastewater sludge, and 3) treated wastewater effluent prior to dilution with cooling water (UPIU 1989). The study also collected data on waste treatment operations, waste discharge characteristics, and sludge disposal information.

Appendix A to this report presents 2378 TCDD and 2378 TCDF concentrations on a dry basis in bleached pulp samples for the 104 plants.

The 2378 TCDD concentrations in sulfite pulp were much lower than the kraft pulp concentrations, ranging from 1 ppt to 15 ppt with no detection corresponding to a detection level of 1 ppt (UPIU 1989). This finding confirms the EPA screening studies which showed that the highest level of PCDD/PCDF concentrations were associated with the kraft process. Kraft pulp typically will require more bleaching stages than will sulfite pulp to bring it to the same level of brightness (Kirk-Othmer 1981b).

PEI evaluated the reported concentrations of 2378 TCDD and 2378 TCDF in bleached pulp samples. An analysis of the concentrations in the sludge will be presented in a separate report. For the purpose of calculating mean and median TEQ concentrations, PEI assumed the concentrations of samples in which 2378 TCDD and 2378 TCDF were not detected to be half of the detection level, and samples which were not quantified were rejected. The results of this analysis are presented in Table 2-5. The low and high plant TEQs provide the data points for the lower and upper ranges of 2378 TCDD and 2378 TCDF concentrations, used for the exposure and risk assessment estimates in this report.

It must be noted that the concentrations of 2378 TCDD and 2378 TCDF measured in pulp and papermaking operations do not necessarily represent worker exposure to these compounds. The data collected from the 104-Mill Study are used in Section 3 for estimating occupational exposures. Worker exposure depends on a variety of conditions (e.g., engineering controls, personal protective equipment, work practices) which are addressed in Section 3.

TABLE 2-5. SUMMARY OF TEQ AND CORRESPONDING 2378 TCDD AND 2378 TCDF CONCENTRATIONS IN BLEACHED PULP FOLLOWING FINAL STAGE OF BLEACHING (104-MILL STUDY)<sup>a</sup> (ppt)

| No. of samples   | TEQ                |      |        | 2378 TCDD range | 2378 TCDF range |
|------------------|--------------------|------|--------|-----------------|-----------------|
|                  | Range <sup>b</sup> | Mean | Median |                 |                 |
| 219 <sup>c</sup> | 0.13(29)-311(2)    | 17.0 | 6.9    | 0.10-49         | 0.25-2620       |

<sup>a</sup> Information furnished by U.S. Environmental Protection Agency, Washington, D.C., based on 104-mill survey; updated results provided in computer diskette form. Concentrations reported on a dry basis.

<sup>b</sup> Values in parentheses are percent contributors due to 2378 TCDD.

<sup>c</sup> 2378 TCDD was not detected in 39 samples. 2378 TCDF was not detected in 10 samples.

#### 2.2.2.3 Analyses of Paper Products--

The National Council of the Paper Industry for Air and Stream Improvement (NCASI) has performed some preliminary analyses for 2378 TCDD and 2378 TCDF in composites of several bleached pulp-based products. Because of the limited number of samples analyzed in the NCASI effort, 2378 TCDD and 2378 TCDF concentrations in the pulp from the comprehensive 104-Mill Study were used for all exposure estimation calculations found in Section 3.

### 2.3 PULP AND PAPER INDUSTRY WORKFORCE CHARACTERIZATION

In 1986, the paper and allied products industry employed over 674,000 people, of which approximately three-fourths were directly involved in pulp and paper production (OTA 1989). Table 2-6 summarizes the total number of employees and production workers in 1985 in the various paper and allied product categories. Both integrated and nonintegrated paper mills are included in Table 2-6. Some data on the number of workers in the pulp and paper industry were also obtained from the National Occupational Exposure Survey (NOES); however, the NOES data only included a limited number of

plants, making the data incomplete. As Table 2-6 shows, over 75 percent of the employees in the industry are production workers. Not all of these production workers, however, are exposed to PCDDs and PCDFs; the exposure varies for different job categories. Worker job descriptions and characteristics are discussed herein for the areas/process operations where exposure can occur: brown stock washing, bleaching, papermaking and finishing, pulp-drying, and paper and pulp converting. It is important to note that job categories and descriptions vary considerably throughout the industry depending on equipment layout, degree of automation, and complexity.

TABLE 2-6. TOTAL EMPLOYEES AND PRODUCTION WORKERS IN THE ENTIRE PAPER AND ALLIED PRODUCTS INDUSTRY, 1985<sup>a</sup>

| Industry group                         | Total number of employees | Production workers |
|--|---------------------------|--------------------|
| Pulp mills                             | 16,000                    | 12,000             |
| Paper mills, except building paper     | 132,000                   | 102,000            |
| Paperboard mills                       | 54,000                    | 41,000             |
| Miscellaneous converted paper products | 211,000                   | 161,000            |
| Paperboard containers and boxes        | 188,000                   | 143,000            |
| Building paper and board mills         | 4,000                     | 3,000              |
| Total                                  | 604,000                   | 462,000            |

<sup>a</sup> (Census 1987)

Generally, pulp and papermaking mills operate 24 hours per day, 4 shifts per 24-hour day (one shift is off), 7 days per week. Paper converting operations usually shut down at night and on weekends (Soklow 1984).

The workforce characterization in kraft pulp and paper mills has not been fully studied. A limited amount of information was obtained from such sources as EPA literature, NIOSH databases, industry data, and various

industrial contacts. However, numerous additional assumptions were needed to calculate the number of workers in each job category. It was assumed that the number of workers in kraft pulp mills was proportional to the ratio of the amount of bleached pulp to the total amount of pulp produced. Other assumptions are stated in the respective sections.

### 2.3.1 Brown Stock Washing

In brown stock washing operations, the potential for PCDD/PCDF exposure exists only if paper machine white waters, which have been used in the processing of bleached pulp, are recycled. However, the recycling of white waters is a rare practice in brown stock washing operations throughout the pulp and paper industry. The job categories in brown stock washing operations which could have the greatest potential for exposure to PCDDs and PCDFs are the wash and screen room operators, pulp tests, and utility employees. Table 2-7 summarizes the number of these employees per shift and pulp production at mills surveyed in a study conducted by the National Institute for Occupational Safety and Health (NIOSH 1983).

The wash and screen room operators monitor and control operations of washer lines, screens, filtrates, and high-density storage tanks (Soklow 1984). The number of wash and screen operators in a plant may range from 0 to 4, averaging 1 to 2 per shift (NIOSH 1983).

Pulp testers are responsible for retrieving and analyzing production area samples. Samples are usually analyzed in laboratory areas located away from the production area such as a wash/screen control room (Soklow, 84). The number of testers per shift may range from 0 to 3, but is usually 1 (NIOSH 1983).

TABLE 2-7. PULP PRODUCTION AND NUMBER OF WORKERS IN BROWN STOCK WASHING AREA PER SHIFT AT MILLS SURVEYED IN A NIOSH STUDY<sup>a</sup>

| Mill No. | Pulp production (tons/day) | Wash and screen operator | Pulp tester    | Utility employee |
|----------|----------------------------|--------------------------|----------------|------------------|
| 1        | 800                        | 1 <sup>c</sup>           | 1              | 1                |
| 8        | 250                        | 1                        | 1              | 1                |
| 11       | NA <sup>b</sup>            | 4 <sup>d</sup>           | 2 <sup>e</sup> | -                |
| 20       | 1,050                      | 2                        | 1              | -                |
| 26       | 1,200                      | 2                        | 1              | -                |
| 29       | 1,300                      | -                        | 3 <sup>f</sup> | -                |
| 33       | 100                        | -                        | -              | -                |
| 36       | NA <sup>b</sup>            | 1                        | 1              | -                |
| 38       | 950                        | 1                        | 1              | 1                |

<sup>a</sup> (NIOSH 1983)

<sup>b</sup> NA = Not available.

<sup>c</sup> Also responsible for bleach plant.

<sup>d</sup> Wash room operator, two helpers, and a screen room operator.

<sup>e</sup> Pulp tester (brown stock washers, refiners) and stock sampler (digester).

<sup>f</sup> Collect and analyze samples from pulp mill and bleach plant.

Utility employees are responsible for keeping the pulp mill clean, conducting routine maintenance, and assisting the operators (EPA 1988). The number of utility employees per shift may range from 0 to 1 (NIOSH 1983).

#### 2.3.2 Bleaching Operations

In the bleaching operations, PCDDs and PCDFs are formed through the use of chlorine or chlorine derivatives, and thus are expected to be at their highest concentrations in the pulp and papermaking process. Four major worker activities include: 1) process monitoring and control; 2) manual operation, and adjustment of equipment, or inspection; 3) process quality control sampling and testing; and 4) housekeeping and spill cleanup (NIOSH 1983).

Table 2-8 presents staffing arrangements, workforce size, production data, and job task assignments for bleaching operations at mills surveyed during a NIOSH study (NIOSH 1983). Table 2-8 confirms the wide variety of job descriptions/categories found throughout the paper industry. Many of the job responsibilities are performed by workers in different job categories, but no two bleach plant workers perform the exact same duties. This overlap is found throughout the pulp and paper industry. The operator is solely responsible for process monitoring and control but is assisted by equipment tenders and helpers for equipment inspection and operation. Quality control testing is performed primarily by helpers, although assistant operators may be assigned to this task. Housekeeping and spill cleanup operations are usually done by utility employees, although operators and assistant operators may perform these functions in small mills. The total number of production workers per shift ranges from 2 to 5 (NIOSH 1983). The bleach plant population potentially exposed to dioxins and dibenzofurans is estimated to be



TABLE 2-8. STAFFING ARRANGEMENTS, WORKFORCE SIZE, PRODUCTION DATA, AND JOB TASK ASSIGNMENTS PER SHIFT FOR BLEACHING OPERATIONS AT MILLS SURVEYED IN A NIOSH STUDY<sup>a</sup>

| Mill No. | Staffing arrangement  | Total No. of production workers per shift <sup>c</sup> | Pulp production (tons/day) | No. of bleach lines | Bleaching sequence(s) | Major job task assignments     |                                    |                         |  |  |
|----------|---|--|----------------------------|---------------------|-----------------------|--------------------------------|------------------------------------|-------------------------|--|--|
|          |   |  |                            |                     |                       | Process Monitoring and Control | Equipment Inspection and Operation | Quality Control Testing | Housekeeping and Spill Cleanup                 |  |
| 01       | Combined staff for bleaching and bleach chemical handling                         | 4-5  | 800                        | 1                   | CEDED                 | Operator                       | Operator and 2nd equipment tender  | Pulp mill 1st helper    | Pulp mill utility worker                       |  |
| 10       | Combined staff for bleaching and bleach chemical handling                         | 3  | 225                        | 1                   | CEHD                  | Operator                       | Operator and bleach plant helper   | Bleach plant helper     | Bleach plant utility worker                    |  |
| 12       | Combined staff for bleaching and bleach chemical handling                         | 2  | 550                        | 1                   | CEDED                 | Operator                       | Operator or assistant operator     | Assistant operator      | Operator or assistant operator                 |  |
| 22       | Combined staff for bleaching, washing, and chemical handling                      | 3  | NA <sup>d</sup>            | 1                   | CEH                   | Operator                       | Operator and assistant operator    | Assistant operator      | Utility worker                                 |  |
| 25       | Combined staff for bleaching and bleach chemical handling                         | 3  | 1,200                      | 2                   | CEHD, CEHDD           | Operator                       | Assistant operator                 | Bleach plant tester     | Assistant operator or pulp mill utility worker |  |
| 30       | Separate staff assigned strictly to bleach plant                                  | 2  | 620                        | 1                   | CEHD                  | Operator                       | Operator and bleach plant helper   | Helper                  | Operator or pulp mill utility worker           |  |
| 35       | Separate staff assigned strictly to bleach plant                                  | 3  | 500                        | 1                   | CEHD                  | Operator                       | Assistant operator                 | Tester                  | Assistant operator                             |  |
| 37       | Separate staff operates two bleach lines; one worker does chemical handling tasks | 5  | Proprietary                | 2                   | CEHDED                | Operators crew leader          | Operator                           | Operator                | Utility relief operator                        |  |

<sup>a</sup> (NIOSH 1983)

<sup>b</sup> All mills use kraft pulping process except Mill No. 22 which uses the sulfite pulping process.

<sup>c</sup> Excludes supervisory and maintenance personnel.

<sup>d</sup> NA = Not available.

1,300 workers total, based on the assumption that there are three employees on each of the four shifts within the 104 mills.

### 2.3.3 Papermaking and Finishing

In this stage, additives such as coatings, colorings, or sizing agents can be mixed with the pulp stock. Job categories potentially exposed to PCDDs and PCDFs include operators, assistants, and utility employees. Table 2-9 presents the estimated number of workers per shift for general papermaking operations. The number of workers per shift in the papermaking operations will vary depending on 1) number and location of paper machines, coaters, and slitters/rewinders; 2) the type and complexity of wet-end operations; 3) the complexity, speed, and extent of automation of papermaking equipment; and 4) the type, number, and complexity of the dry-end operations (NIOSH 1983).

Wet-end additives/stock preparation operators are responsible for operating and monitoring the equipment during the following types of activities: dry pulp dissolving; beating, refining, thickening, cleaning, and blending of pulps; preparing additives such as sizes, fillers, and covering agents; and mixing and blending of ingredients. Operators in the coating preparation category are responsible for the preparation of the coatings, unloading the raw materials, and monitoring the system. Coating ingredients include defoamers, sodium hydroxide, ammonia, and latex. The paper machine wet-end operators perform web forming and water removal by suction and/or pressing in a Fourdrinier or cylinder machine which removes most of the water from the formed sheet (Soklow 1984).

TABLE 2-9. NUMBER OF WORKERS IN PAPERMAKING OPERATIONS<sup>a</sup>

| General process operations               | General job categories              | Estimated No. of workers per shift (per machine) |
|--|-------------------------------------|--|
| Wet-end additives and stock preparations | Operator (beater man)               | 1  |
|  | Assistant                           | 1-2  |
|  | Utility                             | 0-1  |
| Coating preparation                      | Operator                            | 1  |
|  | Assistant                           | 1-2  |
|  | Utility                             | 0-1  |
| Paper machine wet-end                    | Machine tender                      | 1  |
|  | Assistant                           | 0-1  |
|  | Utility                             | 0-1  |
| Paper machine dry-end                    | Back tender                         | 1  |
|  | Splitter/winder operator (3rd hand) | 1  |
|  | Assistants (4th/5th hands)          | 1-3  |
|  | Coater operator                     | 1  |
|  | Utility                             | 0-2  |
|  |                                     |  |
| Off-machine coating                      | Operator                            | 1  |
|  | Assistant                           | 1  |
|  | Utility                             | 0-2  |

<sup>a</sup> (NIOSH 1983)

Dry-end paper machine operators are responsible for web drying, on-machine coating and drying, reeling, on-machine calendering, slitting/rewinding, quality control testing, and packaging and shipping. Drying operations utilize hot air circulated under a hooded ventilation system for the final drying step. The back tender is responsible for the drying, reeling, and calendering operations. The third-hand's duties include operating the winder and finishing the rolls for wrapping. The third-hand spends the majority of his time at the winder control console; however, the third-hand also performs the area blowdown operations (cleaning of equipment to remove excess paper dust). Fourth- and fifth-hands do various tasks including threading paper, preparing cores, and assisting with the blowdown (Soklow 1984).

Off-machine coating operations include application of the coating formulation, paper drying, and rewinding of the paper into rolls. Operators are responsible for monitoring the process, checking paper quality, assisting the utility personnel with loading or unloading rolls of coated paper, and cleaning of the dryer during upsets (Soklow 1984).

The paper mill population potentially exposed to PCDDs and PCDFs is estimated to be 32,000 workers total, based on the assumption that there are two machines per facility, with 18 people per each of the four shifts working at each machine in the 221 facilities processing bleached kraft and sulfite pulp. The number of facilities processing bleached pulp was estimated to be proportional to the quantity of bleached pulp production.

#### 2.3.4 Pulp Drying

In the drying operations there are typically three to five workers per shift, including one to three equipment operators, a fork-truck driver, and a utility person. No information was available on the total number of pulp

drying workers. The number of pulp drying operators potentially exposed to PCDDs and PCDFs was estimated to be 240 people assuming four workers in each shift of the 15 mills that use pulp drying (Census 1988). Operators in the drying stage of pulp production are responsible for monitoring the equipment, weighing the pulp sheets, off-loading and stacking the pressed pulp sheets, and cutting and baling the dry pulp. Fork-truck drivers are responsible for removing the finished bales of pulp and stacking them for shipment. The utility operators clean up any spills and assist the operators in keeping the production area clean (McCubbin 1989).

#### 2.3.5 Converting Operations

Converting operations transform paper into end products such as paper towels, cardboard boxes, and typing paper. Since there is a wide variety of paper products made by converting operations, a generalized workforce characterization is not reported in the literature.

Of the 304,000 paper converting workers, 129,000 workers are estimated to be potentially exposed to PCDDs and PCDFs based on the Bureau of Census data from Table 2-7 and the assumption that the number of workers is proportional to the amount of bleached paper produced.

#### 2.3.6 Nonwoven Operations

Operators in the nonwoven industry are responsible for machine operation and monitoring the system, raw material handling, quality control testing, and general housekeeping. Operators load the pulp rolls onto the unwinder and operate the machinery which includes the unwinder, the hammer mill, and the product packaging and forming equipment. The newer nonwoven plants are automated; however, the older plants may require manual feeding of the hammer mill. Nonwoven products made from pulp are part textile and part pulp. For the exposure calculations, PEI assumed that nonwovens are made from 50 percent

pulp/50 percent textiles. The products from nonwoven operations vary from diapers to surgical gowns, but are all treated as a single operation for this report. Typically, there are two to four operators per shift for each finished-product machine (Nonwovens 1989). No precise information was available on the total number of workers in the nonwoven industry; however, the number of workers has been estimated to be more than 15,000 workers (Cunningham, 1990). Exposures are assumed to be similar regardless of the product manufactured (i.e., diapers, surgical gowns, etc.). Although not evaluated in this report, a potential for worker exposure exists in the manufacture of rayon or cellulose for use in textile fibers, filters, and food additives.

#### 2.3.7 Commercial Users

Commercial users of paper products include almost all workers. Some occupational classifications where workers are exposed for large portions of their work day include lawyers, computer programmers, secretaries, accountants, librarians, teachers, architects, postal workers, printers, and other government workers. Several types of paper products are utilized in various ways which makes the workforce characterization difficult. According to information from the Bureau of Census, over 50 million workers in the United States have occupations which involve handling bleached paper products. Table 2-10 presents the number of workers in each job category who may be exposed to bleached paper products.

Medical workers who use nonwoven products containing bleached pulp include doctors, nurses, dentists, and other workers involved in health maintenance and diagnosing. These workers may wear nonwoven garments or breathe through nonwoven face masks for several hours each day. Table 2-10

TABLE 2-10. NUMBER OF COMMERCIAL USERS OF PAPER AND NONWOVEN PRODUCTS<sup>a</sup>

| Occupation   | Total employed    |
|--|-------------------|
| Paper user   |                   |
| Managerial and professional specialty                                  |                   |
| Accountants and auditors   | 1,255,000         |
| Architects   | 135,000           |
| Teachers, college and university                                       | 661,000           |
| Teachers, prekindergarten, kindergarten<br>elementary, and secondary   | 3,587,000         |
| Librarians, archivists, and curators                                   | 219,000           |
| Lawyers and judges   | 707,000           |
| Management   | <u>18,404,000</u> |
| SUBTOTAL   | 24,968,000        |
| Technical, sales, and administrative support                           |                   |
| Computer programmers   | 527,000           |
| Sales representatives and workers                                      | 9,847,000         |
| Computer operators   | 911,000           |
| Secretaries, stenographers, and typists                                | 5,004,000         |
| Records and financial records processing                               | 3,313,000         |
| Duplicating and mail/message distribution                              | 1,030,000         |
| Miscellaneous administrative support                                   | <u>3,071,000</u>  |
| SUBTOTAL   | 23,703,000        |
| Nonwovens user   |                   |
| Medical workers (dentists, physicians, dentists,<br>registered nurses) | 2,895,000         |
| TOTAL  | <u>51,566,000</u> |

<sup>a</sup> (Census 1988)

presents the number of medical workers who may be exposed to bleached pulp in nonwoven products.

Table 2-11 summarizes the overall number of workers (by industry segment and job category) exposed to bleached pulp and paper products. These values will be used in Section 3 for the population risk calculations.

TABLE 2-11. NUMBER OF WORKERS IN THE  
PULP AND PULP PRODUCTS JOB CATEGORIES

| Job category                           | No. of workers |
|--|----------------|
| Pulp mill                              |                |
| Pulp manufacture                       | 1,300          |
| -Bleach operators                      | 434            |
| -Pulp testers                          | 433            |
| -Utility operators                     | 433            |
| Pulp drying                            | 240            |
| -Operators                             | 160            |
| -Utility workers                       | 80             |
| Paper mill                             |                |
| Paper and paperboard manufacture       | 32,000         |
| -Wet-end operator                      | 10,667         |
| -Dry-end operator                      | 12,445         |
| -Utility operator                      | 8,888          |
| Converting operations                  |                |
| Paper converting operations            | 68,000         |
| -General worker                        |                |
| Paperboard converting operations       | 61,000         |
| -General worker                        |                |
| Nonwovens production (pulp converting) | 15,000         |
| -General worker                        |                |
| Commercial users                       |                |
| Paper and paperboard (see Table 2-10)  | 48,671,000     |
| Nonwovens (see Table 2-10)             | 2,895,000      |



### SECTION 3

#### WORKER EXPOSURE

Although considerable data have been collected on concentrations of 2378 TCDD and 2378 TCDF, for pulp, sludge, and wastewaters in the pulp and paper industry, no inhalation or dermal exposure data for 2378 TCDD and 2378 TCDF are currently available. This is in part because of the lack of a validated sampling and analytical method for measuring worker exposures to these chemicals. Furthermore, little information is available on the effectiveness of engineering controls or the use of personal protective equipment in this industry. PEI, therefore, had to resort to exposure modeling techniques based on numerous assumptions in order to estimate worker exposure to 2378 TCDD and 2378 TCDF.

Pulp and paper mill workers may be exposed to 2378 TCDD and 2378 TCDF either through dermal contact with wet or dry pulp, paper, or bleaching filtrates, or through inhalation of volatilized 2378 TCDD/2378 TCDF or particulate containing these chemicals. The source of particulates is paper dust generated from paper cutting, rolling, or packaging operations. Mists from the mechanical handling of wet pulp may be generated, but there is less potential for aerosol generation in the pulp mill than there is for volatilization (Sullivan 1989).

The estimates of inhalation exposures due to volatilized 2378 TCDD/2378 TCDF presented in this section are relatively low because of the low vapor pressures of these chemicals. In addition, TCDDs/TCDFs have a tendency to

preferentially bind with organic matter. No attempt was made to compensate for 2378 TCDD/2378 TCDF affinity for organic materials.

Some exposure estimates are based on the assumption that TCDDs, TCDFs, pulp and water mixtures have two phases--an aqueous phase and a solid or pulp phase. Furthermore, TCDDs and TCDFs are assumed to reside only in the aqueous portion of the mixture. The aqueous phase is assumed to consist only of TCDDs, TCDFs, and water and is assumed to behave as an ideal solution. Consequently, the estimates presented here represent worst-case values.

NIOSH has recently developed a sampling and analytical method for PCDDs and PCDFs and is planning an extent-of-exposure study at 4 kraft pulp mills. To date, NIOSH has taken five samples at one pulp and paper mill that uses both softwood and hardwood; the sampling effort at other mills will depend on the analytical results from the study at the first mill.

### 3.1 POTENTIAL FOR WORKER EXPOSURE

The potential for inhalation and dermal exposures from pulp and paper manufacturing, converting, and nonwovens operation will vary in the industry, depending on the worker job category, whether the process is enclosed, extent of automation, and equipment layout.

#### 3.1.1 Pulp Manufacture

In pulp manufacturing operations, the potential for exposure to PCDDs and PCDFs exists primarily in the bleaching operations. In brown stock washing operations, exposure to PCDDs and PCDFs occurs if water used for these operations is recycled paper machine white waters containing PCDDs and PCDFs formed during bleach operations. The most common wash method, however, is effluent from the filters and fresh hot water which are not likely to contain PCDDs, PCDFs, or their precursors. Worker activities in brownstock

operations include servicing of the brownstock washers and screens, sample collection and testing, and general plant maintenance, which usually involves cleanup of spills. Brown stock washers are well ventilated, with exhausts through canopy hoods or full enclosures. These hoods are necessary to control workplace contamination with hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide to below regulatory limits. For hydrogen sulfide, the acceptable Occupational Safety and Health Administration (OSHA) ceiling concentration is 20 ppm, and the acceptable OSHA maximum peak concentration for an 8-hour shift is 10 ppm over a maximum duration of 10 minutes. For methyl mercaptan, the NIOSH recommended 15-minute ceiling value is 0.5 ppm; the OSHA 8-hour revised Permissible Exposure Limit (PEL) is 0.5 ppm.

Most kraft pulping processes are highly automated and, consequently, the operators spend considerable portions of each shift inside control rooms (NIOSH 1983). In brownstock washing operations with no isolated control room in the washer area, operators may spend essentially the entire shift in the production area, usually at operating consoles (Soklow 1984). The percentage of time spent in the control room ranges from 0 to 90 percent for operators, 50 to 90 percent for testers, and 30 to 40 percent for utility employees (NIOSH 1983). Based on a NIOSH study, average times spent in the control rooms for workers involved in brownstocking were 65 percent, 75 percent, and 33 percent for the operators, testers, and utility employees, respectively. Since the practice of recycling white waters is rarely done in brownstock washing operations, exposures are not estimated for workers in this area because it is unlikely that these workers will be exposed to 2378 TCDD/2378 TCDF.

The number of bleach plant workers potentially exposed to PCDDs and PCDFs and their job descriptions depend upon the process size, degree of automation, plant layout and equipment, and integration of bleach chemical handling and preparation operations. Various bleaching process characteristics may reduce the potential for exposure to PCDDs and PCDFs. Ventilation of workplace areas that contain chlorine and chlorine dioxide towers, washers, and washer filtrate tanks potentially reduce worker inhalation exposure to PCDDs and PCDFs. Chlorine and chlorine dioxide towers are often installed outdoors for greater ventilation and isolation; however, the actual bleaching process is a closed system with limited potential for leaks. Chlorine alarms are installed in the pulp bleaching building and usually set to go off at 1 ppm, which is the revised OSHA Short-Term Exposure Limit (STEL) over 15 minutes for chlorine. The revised OSHA PEL for chlorine is 0.5 ppm. These engineering controls would also limit exposure to PCDD/PCDF vapors in the building. Rinsing operations often occur in open washers. Consequently, the potential exists for vapor and dermal exposure. Closed pulp conveyance systems are typically used throughout the industry in the post-chlorination, post-hypochlorite, and post-chlorine dioxide stages. Sampling of the wet bleached pulp or spill cleanup provides potential for worker dermal exposure unless proper personal protective equipment is worn. Workers can often reach into the wash stream to gather samples of bleached or partially bleached wet pulp. The above-mentioned controls could greatly minimize the potential for inhalation and dermal exposure to workers involved in the bleaching process. Furthermore, worker isolation through the use of isolated control rooms is prevalent throughout the industry. Workers are generally provided with escape respirators in case of a chlorine leak, but

typically respirators are not used in everyday bleach plant operator activities (Soklow 1984). The amount of time per shift typically spent in the control room ranges between 75 and 90 percent for operators, 60 and 75 percent for helpers, and less than 20 percent for utility workers (NIOSH 1983). The following is an estimation of both inhalation and dermal exposures for each pulp mill job category.

#### 3.1.1.1 Level of Inhalation Exposure--

In the pulp mill, there are three job categories of workers (bleach plant operators, pulp testers, and utility operators) who are potentially exposed to PCDDs and PCDFs through inhalation. These workers spend approximately 75, 25, and 20 percent of their shifts in the control room.

In the manufacture of pulp, only vapors generated from volatilization of the PCDDs and PCDFs constitute a potential route for inhalation exposure. No pulp dust is generated at this point in the production process. Pulp dust may be generated during pulp drying operations, which are discussed in the next subsection. There are no existing data available to determine inhalation exposure to 2378 TCDD/2378 TCDF vapors during pulp manufacturing. In the absence of exposure monitoring data, PEI estimated worker exposure to 2378 TCDD/2378 TCDF using two different approaches (based on the nature of the worker activities). The first approach utilizes a mass balance model to estimate worker exposure for specific activities (e.g., for pulp testers during sampling). The second approach is applicable for workers in a general area (e.g., bleach plant operators, utility operators) and is based on estimating the maximum 2378 TCDD/2378 TCDF air concentration available for inhalation based on their partial pressures. These partial pressures are calculated by assuming that TCDD, TCDF, and pulp water solutions behave as

ideal mixtures. Specific details of the approaches are discussed under each scenario for which worker exposures are estimated.

There are many mass balance models available for estimating worker exposure. Table 3-1 presents some of the mass balance models (equations and solutions) which can be used to estimate contaminant concentrations in confined spaces. These models only differ by factors added to or subtracted from the first mass balance equation in Table 3-1. The most common models used to describe workplace contaminant concentrations are equations representing the mass balance of a contaminant as it is generated and removed from an enclosed space. Clement (Clement 1982) recommends using the fourth model listed for situations with generation sources and ventilation rate. The solution of this mass balance model can be simplified by assuming generation rate and ventilation rate are constant and steady state is reached. Under these conditions, the fourth equation in Table 3-1 reduces to:

$$C = G/kQ \quad \text{Equation 2}$$

where: C = vapor concentration, g/m<sup>3</sup>  
G = generation rate, g/sec  
k = mixing factor, unitless  
Q = ventilation rate, m<sup>3</sup>/sec

The simplest equation describing the generation rate for a volatile liquid (Thibodeaux 1979) is presented in Equation 3.

$$G = \frac{M K A (P^\circ - P)}{R T} \quad \text{Equation 3}$$

where: G = generation rate, g/sec  
M = molecular weight, g/mole  
K = gas transfer coefficient, cm/sec  
A = surface area of the pure component, cm<sup>2</sup>  
P<sup>°</sup> = vapor pressure of the pure component, atm  
P = actual partial pressure of the vapor in the gas phase, atm  
R = universal gas constant (82.05 cm<sup>3</sup> atm/mole degrees Kelvin)  
T = temperature, K

TABLE 3-1. MASS BALANCE MODELS  
(Clement 1981)

| Mass balance equation                               | Solution  | Equation |
|---|---|----------|
| $V \frac{dC}{dt} = - CQ$                            | $C = C_0 e^{-(Q/V)t}$   | (1)      |
| $V \frac{dC}{dt} = - kCQ$                           | $C = C_0 e^{-k(Q/V)t}$  | (2)      |
| $V \frac{dC}{dt} = G - CQ$                          | $C = G/Q + (C_0 - G/Q)e^{-(Q/V)t}$  | (3)      |
| $V \frac{dC}{dt} = G - kCQ$                         | $C = G/Q + (C_0 - G/Q)e^{-k(Q/V)t}$   | (4)      |
| $V \frac{dC}{dt} = G + C_i Q - CQ$                  | $C = C_0 e^{-(Q/V)t} + (C_i + G/Q) (1 - e^{-(Q/V)t})$   | (5)      |
| $V \frac{dC}{dt} = G + kC_i Q - kCQ$                | $C = C_0 e^{-k(Q/V)t} + (C_i + G/Q) (1 - e^{-k(Q/V)t})$                                       | (6)      |
| $V \frac{dC}{dt} = G + C_i Q_i - CQ_i - CEQ_r$      | $C = C_0 e^{-((Q_i + EQ_r)/V)t} + \frac{C_i Q_i + G}{Q_i + EQ_r} (1 - e^{-((Q_i + E_r)/V)t})$ | (7)      |
| $V \frac{dC}{dt} = G(t) + kC_i Q_i - kCQ_i - KEQ_r$ | Variable--depends on the function $G(t)$  | (8)      |

The generation rate is a function of 1) the difference between the equilibrium vapor pressure ( $P^\circ$ ) of the substance at ambient temperature and the actual partial pressure ( $P$ ) of the vapor present in the gas phase, 2) the surface area of the liquid in contact with the air ( $A$ ), and 3) the overall mass transport coefficient ( $K$ ). For most applications,  $P^\circ$  is greater than  $P$ , so  $G$  is effectively independent of the ambient gas phase concentration (i.e.,  $P$  is negligible).

Combining Equations 2 and 3 and assuming  $P$  is negligible results in Equation 4. Since the units in Equations 2 and 3 are different, a constant was calculated to convert the units of Equation 4 into ppm. This factor is based on converting  $m^3/sec$  into  $ft^3/min$  and  $g/m^3$  into ppm, and dividing by the universal gas constant ( $R$ ). The mass transfer coefficient ( $K$ ) in Equation 4 varies with the intrinsic properties of the liquid and properties of the medium into which the liquid evaporates. A typical mass transfer coefficient varies by a constant times the diffusion coefficient to some power. Since the mass transfer coefficients ( $K$ ) were not available in the literature for 2378 TCDD and 2378 TCDF, Equation 5 was used to estimate the mass transfer coefficients. The derivation of this equation is presented in Clement 1982. In addition, the vapor pressure of the pure component is replaced by the partial pressure of 2378 TCDD/2378 TCDF in the mixture. Equation 6 presents the equation for calculating partial pressure based on Raoult's Law. The weight fraction of the 2378 TCDD/2378 TCDF in the dry pulp is available. However, the mole fraction of 2378 TCDD and 2378 TCDF on a wet basis is required for Equation 6.



$$C_v = \frac{6.3 \times 10^5 K A P_a}{k Q T} \quad \text{Equation 4}$$

$$K = 0.83 (18/M)^{1/3} \quad \text{Equation 5}$$

$$P_a = P^\circ X_a \quad \text{Equation 6}$$

where  $C_v$  = concentration of 2378 TCDD/2378 TCDF in the vapor, ppm

$K$  = gas mass transfer coefficient, cm/sec

$A$  = surface area,  $\text{cm}^2$

$P_a$  = partial pressure of a component, atm

$k$  = mixing factor, unitless

$T$  = temperature, K

$Q$  = ventilation rate,  $\text{ft}^3/\text{min}$

$M$  = molecular weight, g/g-mole

$P^\circ$  = vapor pressure of pure component, atm

$X_a$  = mole fraction 2378 TCDD/2378 TCDF in the wet pulp

Exposure estimates during pulp drying are based on the assumption that TCDDs, TCDFs, pulp and water mixtures have two phases--an aqueous phase and a solid or pulp phase. Furthermore, TCDDs and TCDFs are assumed to reside only in the aqueous portion of the mixture. The aqueous phase is assumed to consist only of TCDDs, TCDFs, and water and is assumed to behave as an ideal solution and obey Raoult's Law. It was assumed that TCDDs/TCDFs and water are removed from the pulp at rates that ensure that relative concentrations of these components in the ideal mixture remain constant.

The weight fraction on a dry basis for 2378 TCDD and 2378 TCDF is present in the 104-Mill Study data. However, for the calculation of 2378 TCDD and 2378 TCDF exposure to vapors, the mole fraction of 2378 TCDD and 2378 TCDF on a wet basis is required. There are two steps to convert from a weight fraction on a dry basis to a mole fraction on a wet basis. The first

step is to convert from a weight fraction on a dry basis to a weight fraction on a wet basis. Based on an average pulp composition of 11 weight percent pulp (NIOSH 1983) and the assumption that the aqueous phase contains 2378 TCDD, 2378 TCDF, and water, the weight fraction in the aqueous phase is approximately 0.12 times the weight fraction on a dry basis. The second conversion involves transforming the weight fraction on a wet basis to a mole fraction on a wet basis. The mole fraction in the aqueous phase can then be computed from a knowledge of the molecular weight of water, molecular weight of 2378 TCDD/2378 TCDF, and the weight fraction of 2378 TCDD/2378 TCDF on a wet basis. The mole fraction of 2378 TCDF/2378 TCDF in the aqueous phase is thus approximately 0.06 times the weight fraction of 2378 TCDD/2378 TCDF in the aqueous phase. Thus, the mole fraction of 2378 TCDD/2378 TCDF in the aqueous phase is approximately 0.007 times the weight fraction of 2378 TCDD/2378 TCDF on a dry basis.

The approach for estimating worker inhalation exposure concentrations to 2378 TCDD/2378 TCDF around closed systems in the bleaching area was based on comparison with the OSHA PEL for another chemical (chlorine) handled in the same process area and a knowledge of the vapor pressures of chlorine and 2378 TCDD/2378 TCDF. The airborne concentrations of 2378 TCDD and 2378 TCDF were estimated based on a comparison with the PEL for chlorine, since there are alarms in the bleach processing area for chlorine to limit workers' exposure to this chemical below its PEL. The use of a PEL to estimate inhalation exposures gives a maximum or reasonable worst case workplace concentration. The exposures for the bleach plant operator and utility operator were assumed to be comparable since their job duties require them to be in the bleaching area of the pulping process for a portion of the shift. Therefore, the same

approach was used to estimate inhalation exposure for these job categories; and the empirical equation for this approach is presented in Equation 7:

$$C_v = C_{vc} \times \frac{P_o}{P_c} \quad \text{Equation 7}$$

where  $C_v$  = hourly concentration of 2378 TCDD/2378 TCDF, ppm  
 $C_{vc}$  = 8-hour PEL for chlorine, ppm (0.5 ppm) (Federal Register 1989)  
 $P_o$  = vapor pressure of the pure component at 25 °C, atm  
 $P_c$  = vapor pressure of chlorine at 25 °C, atm (7.9 atm)

The inhalation exposure from volatilization for all job categories is converted from ppm to  $\text{mg}/\text{m}^3$  using the equation presented in Equation 8. This value is substituted into Equation 9 resulting in a daily inhalation exposure ( $I_v$ ) in  $\text{mg}/\text{day}$ .

It is pointed out that all the calculated inhalation exposure levels from volatilization presented in this report are biased high because no consideration is given to the 2378 TCDD/2378 TCDF binding with organic matter and the presence of other chemicals in the matrices that could interfere with the volatilization of the 2378 TCDD/2378 TCDF. No estimates could be either found in the literature or provided by contacts in the field which would allow for quantifying the impact of these interferences on volatilization.

$$C_m = C_v M/V_m \quad \text{Equation 8}$$

$$I_v = C_m \times 1.25 \text{ m}^3/\text{h} \times \text{ED} \quad \text{Equation 9}$$

where  $C_m$  = concentration of 2378 TCDD/2378 TCDF in the vapor,  $\text{mg}/\text{m}^3$

$C_v$  = concentration of 2378 TCDD/2378 TCDF in the vapor, ppm

$M$  = molecular weight, g/mole

$V_m$  = molar volume, liter/mole (24.45 liter/mole at  $T = 25^\circ\text{C}$  and  $P = 760 \text{ mm Hg}$ )

$I_v$  = daily inhalation exposure from volatilization,  $\text{mg}/\text{day}$

$\text{ED}$  = exposure duration, h/day

Table 3-2A summarizes the variables and results from using Equations 4 through 6 and Equations 8 and 9 for the pulp testers. Table 3-2B summarizes the variables and results from using Equations 7 through 9 for the bleach plant and utility operators. The tables present estimated daily exposure to 2378 TCDD and 2378 TCDF for pulp mill workers from volatilization.

The relative toxicity of 2378 TCDF with respect to 2378 TCDD can be determined by calculating toxicity equivalents (TEQ) for the daily exposure. In addition, the percent exposure due to 2378 TCDD can also be calculated. Equation 10 presents the equation for calculating TEQ, while Equation 11 is used for calculating the percent of the exposure due to 2378 TCDD. These equations are found in EPA 1989a. Table 3-3 presents the daily and lifetime average daily TEQ and percent exposure due to TCDD from volatilization for pulp mill workers.

$$DTEQ_v = I_{v_{TCDD}} + 0.1 I_{v_{TCDF}} \quad \text{Equation 10}$$

$$\%TCDD_v = \frac{I_{v_{TCDD}}}{I_{v_{TCDD}} + I_{v_{TCDF}}} \times 100 \quad \text{Equation 11}$$

where:

$DTEQ_v$  = daily toxicity equivalents from volatilization of 2378 TCDD and 2378 TCDF

$I_{v_{TCDD}}$  = daily exposure to 2378 TCDD from volatilization, mg/day

$I_{v_{TCDF}}$  = daily exposure to 2378 TCDF from volatilization, mg/day

$\%TCDD_v$  = percent of the exposure from volatilization due to 2378 TCDD, %

In addition to daily TEQ, the lifetime average daily TEQ (LTEQ<sub>v</sub>) for workers was also calculated. This is presented in Equation 12:

$$LTEQ_v = DTEQ_v \times DY \times LF / (BW \times LE) \quad \text{Equation 12}$$

TABLE 3-2A. ESTIMATED INHALATION EXPOSURE TO 2378 TCDD AND 2378 TCDF FOR PULP TESTERS IN PULP MILLS FROM VOLATILIZATION

| Variable  | 2378 TCDD             |                       | 2378 TCDF             |                       | Reference                          |
|---|-----------------------|-----------------------|-----------------------|-----------------------|------------------------------------|
|   | Low                   | High                  | Low                   | High                  |                                    |
| Surface area of sampling port - pulp tester, cm <sup>2</sup> (A)                  | 40                    | 80                    | 40                    | 80                    | See Table 3-5                      |
| Vapor pressure, atm (P°) @ 25°C   | 9.7x10 <sup>-13</sup> | 9.7x10 <sup>-13</sup> | 1.2x10 <sup>-9</sup>  | 1.2x10 <sup>-9</sup>  | Eitzer and Hites 1986, Podoll 1986 |
| Molecular weight, g/g-mole (M)  | 322                   | 322                   | 306                   | 306                   | EPA 1989b                          |
| Mixing factor, dimensionless (k)  | 0.5                   | 0.5                   | 0.5                   | 0.5                   | See Table 3-5                      |
| Ventilation rate, ft <sup>3</sup> /min (Q)  | 3,000                 | 3,000                 | 3,000                 | 3,000                 | See Table 3-5                      |
| Temperature, K  | 298                   | 298                   | 298                   | 298                   | See Table 3-5                      |
| Weight fraction of 2378 TCDD/2378 TCDF in the pulp, for the pulp tester dry basis | 0.1x10 <sup>-12</sup> | 4.9x10 <sup>-11</sup> | 2.5x10 <sup>-13</sup> | 2.62x10 <sup>-9</sup> | Table 2-5                          |
| Mole fraction of 2378 TCDD/2378 TCDF wet basis (Xa)                               | 7.0x10 <sup>-16</sup> | 3.4x10 <sup>-13</sup> | 1.8x10 <sup>-15</sup> | 1.8x10 <sup>-11</sup> | See Table 3-5                      |
| Gas mass transfer coefficient, cm/s (K)   | 0.32                  | 0.32                  | 0.33                  | 0.33                  | Calculated                         |
| Concentration of 2378 TCDD/2378 TCDF in the vapor, ppm (Cv)                       | 1.2x10 <sup>-26</sup> | 1.2x10 <sup>-23</sup> | 3.9x10 <sup>-23</sup> | 8.1x10 <sup>-19</sup> | Equation 4                         |
| Exposure duration, h/day (ED)   | 1                     | 1                     | 1                     | 1                     | See Table 3-5                      |
| Daily inhalation, mg/day (Iv)   | 2.0x10 <sup>-25</sup> | 1.9x10 <sup>-22</sup> | 6.0x10 <sup>-22</sup> | 1.3x10 <sup>-17</sup> | Calculated                         |

TABLE 3-2B. ESTIMATED INHALATION EXPOSURE TO 2378 TCDD AND 2378 TCDF FOR BLEACH AND UTILITY OPERATORS IN PULP MILLS FROM VOLATILIZATION

| Variable   | 2378 TCDD             |                       | 2378 TCDF             |                       | Reference                                |
|--|-----------------------|-----------------------|-----------------------|-----------------------|--|
|  | Low                   | High                  | Low                   | High                  |  |
| Vapor pressure,<br>atm (P°) @ 25°C                                   | $9.7 \times 10^{-13}$ | $9.7 \times 10^{-13}$ | $1.2 \times 10^{-9}$  | $1.2 \times 10^{-9}$  | Eitzer and Hites<br>1986, Podoll<br>1986 |
| Concentration of<br>2378 TCDD/2378<br>TCDF in the<br>vapor, ppm (Cv) |                       |                       |                       |                       |  |
| - Bleach operator  | $6.1 \times 10^{-14}$ | $6.1 \times 10^{-14}$ | $7.7 \times 10^{-11}$ | $7.7 \times 10^{-11}$ | Equation 7                               |
| - Utility operator   | $6.1 \times 10^{-14}$ | $6.1 \times 10^{-14}$ | $7.7 \times 10^{-11}$ | $7.7 \times 10^{-11}$ | Equation 7                               |
| Exposure dura-<br>tion, h/day (ED)                                   |                       |                       |                       |                       |  |
| -Bleach operator   | 2                     | 2                     | 2                     | 2                     | See Table 3-5                            |
| -Utility operator  | 6                     | 6                     | 6                     | 6                     | See Table 3-5                            |
| Daily inhalation,<br>mg/day (Iv)                                     |                       |                       |                       |                       |  |
| -Bleach operator   | $2.0 \times 10^{-12}$ | $2.0 \times 10^{-12}$ | $2.4 \times 10^{-9}$  | $2.4 \times 10^{-9}$  | Calculated                               |
| -Utility operator  | $6.1 \times 10^{-12}$ | $6.1 \times 10^{-12}$ | $7.2 \times 10^{-9}$  | $7.2 \times 10^{-9}$  | Calculated                               |

where:

LTEQv = lifetime average daily TEQ from volatilization, mg/day-kg  
DTEQv = daily TEQ from volatilization, mg/day  
DY = number of days per year exposed, day/year  
LF = number of years of exposure per lifetime, years/lifetime  
BW = average body weight for a worker, kg  
LE = lifetime expectancy, days/lifetime

The number of years of exposure per lifetime (LF) was assumed to be 40 years and the lifetime expectancy (LE) was assumed to be 25,550 days (i.e., 70 years). The average body weight for male workers (BW) is 70 kg and a female worker is 58 kg (NCASI 1988). PEI assumed that the worker would be in the plant for 250 days per year. Table 3-3 presents the lifetime average daily TEQ. Table 3-4 presents the assumptions and uncertainties of those variables used to calculate lifetime average daily TEQ from daily TEQ.

Table 3-5 presents the assumptions and uncertainties in the variables used to calculate inhalation exposure from volatilization from wet pulp, as presented in Table 3-2. The bleach operators, pulp testers, and utility operators were assumed to be exposed to the PCDD and PCDF vapors during the entire time they are not in the control room.

The following are examples of the calculation procedures used for estimating levels of daily inhalation exposure to 2378 TCDD and 2378 TCDF from volatilization. The first example is for the pulp tester using Equations 4 through 6 and Equations 8 and 9, while the second example is for the bleach plant operator using Equations 7 through 9.

Lower limit of 2378 TCDD inhalation exposure level from volatilization for pulp tester

$$\begin{aligned} P_a &= 9.7 \times 10^{-13} \text{ atm} \times 7.0 \times 10^{-16} \\ &= 6.8 \times 10^{-28} \text{ atm} \end{aligned}$$

TABLE 3-3. ESTIMATED TOXICITY EQUIVALENTS AND PERCENT EXPOSURE DUE TO 2378 TCDD FOR PULP MILL WORKERS FROM VOLATILIZATION

| Job category     | Daily TEQ, <sup>a</sup> mg/day  |                                  | Lifetime average daily TEQ, <sup>a</sup> mg/day-kg |                                  |
|------------------|---------------------------------|----------------------------------|--|----------------------------------|
|                  | Low                             | High                             | Low  | High                             |
| Bleach operators | $2.4 \times 10^{-10}$<br>(0.08) | $2.4 \times 10^{-10}$<br>(0.08)  | $1.4 \times 10^{-12}$<br>(0.08)                    | $1.6 \times 10^{-12}$<br>(0.08)  |
| Pulp testers     | $6.1 \times 10^{-23}$<br>(0.03) | $1.3 \times 10^{-18}$<br>(0.002) | $3.4 \times 10^{-25}$<br>(0.03)                    | $8.6 \times 10^{-21}$<br>(0.002) |
| Utility operator | $7.3 \times 10^{-10}$<br>(0.08) | $7.3 \times 10^{-10}$<br>(0.08)  | $4.1 \times 10^{-12}$<br>(0.08)                    | $4.9 \times 10^{-12}$<br>(0.08)  |

<sup>a</sup> Values in parentheses are percent exposure due to 2378 TCDD.



TABLE 3-4. ASSUMPTIONS AND UNCERTAINTIES IN VARIABLES FOR CALCULATING LIFETIME AVERAGE DAILY TEQ FROM DAILY TEQ

| Uncertainty                                  | Associated assumption   | Reasonable possible variance of assumption | Effects on results                     |
|--|---|--|--|
| Number of days per year workers are exposed. | Workers were assumed to be exposed for 250 days per year (PEI estimate).                      | A maximum exposure duration is 365 days.   | Maximum of 1.5 times greater exposure. |
| Number of years of exposure per lifetime.    | Workers were assumed to be exposed for 40 years (EPA 1989a).                                  |  |  |
| Average body weight of a worker.             | The average body weight of a male worker is 70 kg and a female worker is 58 kg (NCASI 1988c). |  |  |
| Lifetime expectancy of a worker.             | Workers were assumed to live for 70 years (NCASI 1988c).                                      |  |  |

TABLE 3-5. ASSUMPTION AND UNCERTAINTIES IN ESTIMATING INHALATION EXPOSURE TO 2378 TCDD AND 2378 TCDF FOR PULP MILL WORKERS FROM VOLATILIZATION

| Uncertainty   | Associated assumption   | Reasonable possible variance of assumption   | Effects on results  |
|---|---|--|---|
| The surface area where the pulp tester would be exposed to 2378 TCDD and 2378 TCDF.             | The surface area of a sample jar ranges from 40 to 80 cm <sup>2</sup> .   |  |   |
| There is not ideal mixing of 2378 TCDD and 2378 TCDF in the area during sampling.               | The mixing factor was assumed to be 0.5 (Drivas, Simmonds, and Shair 1981) for a typical mixing operation.  | Reasonable range in the mixing factor is 0.1 to 1.0 (Drivas, Simmonds, and Shair 1981).                | Exposure would range from 0.2 to 5 times the exposure level.                                    |
| The ventilation rate in the area where 2378 TCDD and 2378 TCDF exposures occur during sampling. | A typical ventilation rate is 3,000 ft <sup>3</sup> /min (Clement 1982).  | Reasonable range in industrial ventilation rates is 500 to 10,000 ft <sup>3</sup> /min (Clement 1982). | Exposure would range from 0.2 to 3.3 times the exposure level.                                  |
| Temperature in the area where the pulp mill workers would be exposed to 2378 TCDD/2378 TCDF.    | The temperature at the bleaching portion of the process is 25°C (Soklow 1989).  | At the extraction portion of the pulp process the temperature can reach 60°C.                          | Exposure would be 1.1 times the exposure level however, the vapor pressure would also increase. |
| Mole fraction of 2378 TCDD/2378 TCDF for use in Equation 6.                                     | Based on rough approximations, PEI computed mole fraction of the 2378 TCDD/2378 TCDF in the aqueous phase to be equal to 0.007 times the dry weight fraction of the 2378 TCDD/2378 TCDF in the pulp. See text for additional information. |  |   |

(continued)

TABLE 3-5 (continued)

| Uncertainty   | Associated assumption   | Reasonable possible variance of assumption   | Effects on results   |
|---|---|--|--|
| Inhalation exposure duration for bleach plant operator. | The duration of the exposure was assumed to be 2 hours since the operator spends the majority of the shift in the control room (NIOSH 1983).                            | Reasonable range in the duration would be 0.8 to 2 hours since the operator spends 75 to 90 percent of the shift in the control room (NIOSH 1983). | Exposure would range from 0.5 to 1.3 times the exposure level. |
| Inhalation exposure duration for pulp testers.          | The duration of the exposure was assumed to be 1 hour since the worker was assumed to collect samples every 2 hours for 15 minutes during an 8-hour shift (NIOSH 1983). | Reasonable range in the duration would be 0.5 to 2 hours.  | Exposure would range from 0.5 to 2 times the exposure level.   |
| Inhalation exposure duration for utility operator.      | The duration of the exposure was assumed to be 6 hours, since the operator spends the majority of the shift outside the control room (NIOSH 1983).                      | Reasonable range in the duration would be 4 to 8 hours.  | Exposure would range from 0.7 to 1.3 times the exposure level. |

$$K = 0.83 \times (18/322)^{1/3}$$

$$= 0.32 \text{ cm/s}$$

$$C_v = \frac{6.3 \times 10^5 \times 0.32 \text{ cm/s} \times 40 \text{ cm}^2 \times 6.8 \times 10^{-28} \text{ atm}}{0.5 \times 3000 \text{ ft}^3/\text{min} \times 298 \text{ }^\circ\text{K}}$$

$$= 1.2 \times 10^{-26} \text{ ppm}$$

$$C_m = 1.2 \times 10^{-26} \times \frac{322}{24.45}$$

$$= 1.6 \times 10^{-25} \text{ mg/m}^3$$

$$I_v = 1.6 \times 10^{-25} \text{ mg/m}^3 \times 1.25 \text{ m}^3/\text{h} \times 1 \text{ h/day}$$

$$= 2.0 \times 10^{-25} \text{ mg/day}$$

Lower limit of 2378 TCDD inhalation exposure level from volatilization for bleach plant operators

$$C_v = 0.5 \text{ ppm} \times \frac{9.7 \times 10^{-13} \text{ atm}}{7.9 \text{ atm}}$$

$$= 6.1 \times 10^{-14} \text{ ppm}$$

$$C_m = 6.1 \times 10^{-14} \text{ ppm} \times \frac{322}{24.45}$$

$$= 8.1 \times 10^{-13} \text{ mg/m}^3$$

$$I_v = 8.1 \times 10^{-13} \text{ mg/m}^3 \times 1.25 \text{ m}^3/\text{h} \times 2 \text{ h/day}$$

$$= 2.0 \times 10^{-12} \text{ mg/day}$$

The following is an example of the calculation procedure (Equations 10 and 11) for estimating TEQ daily exposure and percent daily exposure due to TCDD for pulp mill workers from volatilization from wet pulp.

Lower limit for TEQ daily exposure and percent daily exposure due to TCDD for bleach plant operators from volatilization

$$\begin{aligned} \text{DTEQv} &= 2.0 \times 10^{-12} \text{ mg/day} + (0.1 \times 2.4 \times 10^{-9} \text{ mg/day}) \\ &= 2.4 \times 10^{-10} \text{ mg/day} \\ \% \text{TCDDv} &= 2.0 \times 10^{-12} \text{ mg/day} / (2.0 \times 10^{-12} \text{ mg/day} + 2.4 \times 10^{-9} \text{ mg/day}) \times 100 \\ &= 0.08\% \end{aligned}$$

The following is an example of the calculation procedure using Equation 12 for estimating lifetime average daily TEQ.

Lower limit for lifetime average daily TEQ to bleach plant operators from volatilization

$$\begin{aligned} \text{LTEQv} &= (3.0 \times 10^{-11} \text{ mg/day} \times 250 \text{ days/yr} \times 40 \text{ years/lifetime}) / \\ &\quad (70 \text{ kg} \times 25,550 \text{ days/lifetime}) \\ &= 1.7 \times 10^{-13} \text{ mg/day-kg} \end{aligned}$$

#### 3.1.1.2 Level of Dermal Exposure--

Dermal exposure levels to 2378 TCDD and 2378 TCDF were computed based on the assumption that workers do not wear any type of gloves that effectively limit exposure to PCDDs and PCDFs. However, in actual practice, some operators may wear chemical-resistant gloves during the handling of the pulp. Since the type of glove used, the extent of glove use, and the frequency of glove replacement could not be determined, consideration in the estimation of dermal exposure could not be given to the degree of protection provided by personal protective equipment.

There are a few different approaches available for estimating dermal exposure. The approach used was that agreed upon by EPA, the Federal Drug Administration, and the Consumer Product Safety Commission (EPA 1989b) for use in this project. This approach considers the partitioning of PCDD/PCDF from the appropriate matrix (e.g., soil, sludges, paper) to a liquid (i.e.,

water, skin oils, urine, blood) and percutaneous absorption of PCDDs and PCDFs from the liquid. In this reference, common assumptions for the assessment of dermal exposure are presented; however, equations for estimating dermal exposures were not provided. CPSC supplied three equations to PEI for estimating dermal exposure (CPSC 1989); these equations are for estimating dermal exposure to pulp, paper, and sludge/soil. The equation for handling wet pulp was selected and is presented in Equation 13.

$$\text{DEW} = \text{DC (ppt)} \times \rho \text{ (mg/cm}^3\text{)} \times \text{FT (cm)} \times \frac{1}{K} \times \text{AD (h}^{-1}\text{)} \times \text{S (cm}^2\text{)} \times \text{ED (h/day)} \quad \text{Equation 13}$$

where:

DEW = dermal exposure from handling wet pulp, mg/day

DC = 2378 TCDD/2378 TCDF concentration in the wet pulp, ppt

$\rho$  = density of the wet pulp, mg/cm<sup>3</sup>

FT = liquid film thickness, cm

K = liquid equilibrium partition coefficient of TCDD and TCDF from water, unitless

AD = absorption coefficient of TCDD/TCDF through the skin, h<sup>-1</sup>

S = skin surface area, cm<sup>2</sup>

ED = exposure duration, h/day

The concentrations reported in the 104 Mill Study for 2378 TCDD and 2378 TCDF were based on dry weight fraction; however, a wet weight fraction for 2378 TCDD and 2378 TCDF was needed for Equation 13. Based on an average pulp composition of 11 weight percent pulp (NIOSH 1983) and the assumption that the aqueous phase contains 2378 TCDD/2378 TCDF and water, the weight fraction in the aqueous phase is 0.12 times the weight fraction on a dry basis.

The bleach plant operator was assumed to spend approximately 75 percent of his shift in the control room which corresponds to 6 hours. The operator leaves the control room to inspect equipment, occasionally collect samples

(typically done by pulp testers), routinely clean up spills, supervise equipment startup and shutdown, and supervise maintenance operations. The major responsibility of this operator is to supervise the pulp mill operation. The density for pulp is assumed to be  $1000 \text{ mg/cm}^3$  and a 2378 TCDD/2378 TCDF liquid film thickness was estimated to be 0.25 mm. Dermal exposure duration was assumed to equal the amount of time the operator spends outside the control room.

The pulp testers spend approximately 75 percent of their shift outside the control room which corresponds to 6 hours. The worker leaves the control room to collect and analyze samples and inspect equipment. Sample collection and testing was assumed to occur for 15 minutes every 2 hours. The range of the dermal exposure duration was based on the time for sampling and analysis and the amount of time the operator spends outside the control room.

The utility operators spend approximately 75 percent of their shift in the bleach plant which corresponds to 6 hours. The utility operator is responsible for cleaning the plant, any spills from the conveyor, and the wash stock from washers and refiners. Dermal exposure duration was based on the time the operator spends outside the control room.

Table 3-6 summarizes the variables and results for dermal exposure for bleach plant operators, pulp testers, utility operators in pulp mills. The relative toxicity of 2378 TCDF with respect to 2378 TCDD can be determined by calculating TEQ. The percent exposure due to 2378 TCDD can also be calculated. Equations 10 and 11 are used to calculate these two variables. In these two equations, the daily inhalation exposure from volatilization (Iv) for 2378 TCDD and 2378 TCDF are replaced with the daily dermal exposure (DEW) for 2378 TCDD and 2378 TCDF. Table 3-7 presents the daily and lifetime

TABLE 3-6. ESTIMATED DERMAL EXPOSURE TO 2378 TCDD AND 2378 TCDF FOR PULP MILL WORKERS

| Variable   | 2378 TCDD             |                       | 2378 TCDF             |                       | Reference     |
|--|-----------------------|-----------------------|-----------------------|-----------------------|---------------|
|  | Low                   | High                  | Low                   | High                  |               |
| 2378 TCDD/2378 TCDF concentration of wet pulp, wet basis, ppt (DC)             | 0.012                 | 5.88                  | 0.03                  | 314                   | See Table 3-8 |
| Density of the pulp, mg/cm <sup>3</sup> ( $\rho$ )                             | 1000                  | 1000                  | 1000                  | 1000                  | See Table 3-8 |
| Liquid film thickness of the pulp, cm (FT)                                     | 0.025                 | 0.025                 | 0.025                 | 0.025                 | See Table 3-8 |
| Liquid equilibrium partition coefficient of TCDD/TCDF from water, unitless (K) | 13,000                | 13,000                | 29,000                | 29,000                | EPA 1989c     |
| Absorption coefficient of PCDD/PCDF through the skin, h <sup>-1</sup> (AD)     | 0.012                 | 0.012                 | 0.012                 | 0.012                 | EPA 1989c     |
| Skin surface area, cm <sup>2</sup> (S)   |                       |                       |                       |                       |               |
| - Bleach operator  | 250                   | 300                   | 250                   | 300                   | See Table 3-8 |
| - Pulp testers   | 650                   | 650                   | 650                   | 650                   | See Table 3-8 |
| - Utility operators  | 1300                  | 1300                  | 1300                  | 1300                  | See Table 3-8 |
| Exposure duration, h/day (ED)  |                       |                       |                       |                       |               |
| - Bleach operators   | 2                     | 2                     | 2                     | 2                     | See Table 3-8 |
| - Pulp testers   | 6                     | 6                     | 6                     | 6                     | See Table 3-8 |
| - Utility operators  | 6                     | 6                     | 6                     | 6                     | See Table 3-8 |
| Dermal exposure, mg/day (DEW)  |                       |                       |                       |                       |               |
| - Bleach operator  | $1.4 \times 10^{-16}$ | $8.1 \times 10^{-14}$ | $1.6 \times 10^{-16}$ | $2.0 \times 10^{-12}$ | Calculated    |
| - Pulp testers   | $1.1 \times 10^{-15}$ | $5.3 \times 10^{-13}$ | $1.2 \times 10^{-15}$ | $1.3 \times 10^{-11}$ | Calculated    |
| - Utility operators  | $2.2 \times 10^{-15}$ | $1.1 \times 10^{-12}$ | $2.4 \times 10^{-15}$ | $2.5 \times 10^{-11}$ | Calculated    |



TABLE 3-7. ESTIMATED TOXICITY EQUIVALENTS AND PERCENT EXPOSURE DUE TO 2378 TCDD FOR PULP MILL WORKERS FROM DERMAL EXPOSURE

| Parameter        | Daily TEQ, <sup>a</sup> mg/day |                              | Lifetime average daily TEQ, <sup>a</sup> mg/day-kg |                              |
|------------------|--------------------------------|------------------------------|--|------------------------------|
|                  | Low                            | High                         | Low  | High                         |
| Bleach operators | $1.5 \times 10^{-16}$<br>(47)  | $2.8 \times 10^{-13}$<br>(4) | $8.6 \times 10^{-19}$<br>(47)                      | $1.9 \times 10^{-15}$<br>(4) |
| Pulp testers     | $1.2 \times 10^{-15}$<br>(47)  | $1.8 \times 10^{-12}$<br>(4) | $6.7 \times 10^{-18}$<br>(47)                      | $1.2 \times 10^{-14}$<br>(4) |
| Utility operator | $2.4 \times 10^{-15}$<br>(47)  | $3.6 \times 10^{-12}$<br>(4) | $1.3 \times 10^{-17}$<br>(47)                      | $2.4 \times 10^{-14}$<br>(4) |

<sup>a</sup> Values in parentheses are percent exposure to 2378 TCDD.

average daily TEQ and percent exposure due to 2378 TCDD from dermal exposure to wet pulp for pulp mill workers. Table 3-8 presents the assumptions and uncertainties in the variables used to calculate the dermal exposures for pulp mill workers in Table 3-6.

The following is an example of the calculation procedure (Equation 13) used for estimating levels of daily dermal exposure for pulp mill workers potentially exposed to TCDDs and TCDFs in the handling of wet pulp. Lower limit of 2378 TCDD dermal exposure level for the bleach plant operator is computed as follows:

$$\begin{aligned} \text{DEW} &= 1.1 \times 10^{-14} \frac{\text{g}}{\text{g}} \times 1000 \text{ mg/cm}^3 \times 0.025 \text{ cm} / 13,000 \times 0.012 \text{ h}^{-1} \times \\ &\quad 250 \text{ cm}^2 \times 2 \text{ h/day} \\ &= 1.3 \times 10^{-16} \text{ mg/day} \end{aligned}$$

### 3.1.2 Pulp Drying

#### 3.1.2.1 Level of Inhalation Exposure--

Inhalation is one route of exposure to PCDDs and PCDFs in pulp-drying operations. During drying of the pulp, vapors are released into the air. It is estimated that the pulp-drying and utility operators may be exposed to PCDDs and PCDFs by inhalation for 2-hours during their shift because their job activities are conducted away from the drying machines for a majority of the shift. The method for estimating inhalation exposure from volatilization for this open operation is based on the maximum partial pressure of 2378 TCDD and 2378 TCDF computed using the ideal gas law. This is a worst-case approach. In this approach, it is assumed that 2378 TCDD and 2378 TCDF are in an ideal solution with water. Pulp was assumed to be a separate solid phase. This approach assumes that the relative amounts of 2378 TCDD/2378 TCDF and water

TABLE 3-8. ASSUMPTIONS AND UNCERTAINTIES IN ESTIMATING DERMAL EXPOSURE TO 2378 TCDD AND 2378 TCDF FOR PULP MILL WORKERS

| Uncertainty   | Associated assumption  | Reasonable possible variance of assumption   | Effects on results   |
|---|--|--|--|
| Weight fraction of 2378 TCDD/2378 TCDF, wet basis (DC).                                 | Based on 11 percent pulp and the presence of 2378 TCDD, 2378 and water only in the aqueous phase, the weight fraction on a dry basis times 0.12 equals weight fraction on a wet basis.   | The pulp concentration at the bleaching stage varies between 10 to 12 percent (NIOSH 1983).  | Exposure would range from 0.9 to 1.1 times the exposure level. |
| Density of the wet pulp   | A 1000 mg/cm <sup>3</sup> density was assumed based on a 11 percent pulp solution with a pulp density of 0.63 to 0.72 g/cm <sup>3</sup> (Grant 1990).  |  |  |
| Liquid film thickness of the wet pulp on the skin                                       | The film thickness was assumed to be 0.25 mm.  | Film thickness for liquids have ranged from 0.01 mm to 0.25 mm (Wong 1983 and Versar 1982).  | Exposure would range from 0.4 to 1.0 times the exposure level. |
| The skin surface area where the bleach plant operator would be exposed to TCDD and TCDF | The exposed skin surface area was estimated by PEI to be 100% of palm and finger surfaces of both hands. The high and low represent the difference between the surface area of a men's and women's hands. The exposed skin surface is 250 cm <sup>2</sup> for females and 300 cm <sup>2</sup> for males (NCASI 1988c). | The exposed skin surface area could potentially include exposure to both hands (front and back). The skin surface area would increase to 1,300 cm <sup>2</sup> (Popendorf 1982). | Exposure would range from 5 to 5.2 times the exposure level.   |

(continued)

TABLE 3-8 (continued)

| Uncertainty  | Associated assumption  | Reasonable possible variance of assumption  | Effects on results   |
|--|--|---|--|
| The skin surface area where the pulp testers would be exposed to TCDD and TCDF     | The exposed skin surface area was estimated by PEI to be one hand (front and back). The skin surface area is 650 cm <sup>2</sup> for one hand (Popendorf 1982).  | The exposed skin surface area could potentially include exposure to both hands (front and back). The skin surface area would increase to 1,300 cm <sup>2</sup> (Popendorf 1982).                              | Exposure would range from 1 to 2 times the exposure level.     |
| The skin surface area where the utility operator would be exposed to TCDD and TCDF | The exposed skin surface area was estimated by PEI to be both hands (front and back). The skin surface area is 1,300 cm <sup>2</sup> for one hand (Popendorf 1983).  | The exposed skin surface area could potentially include exposure to both hands (front and back) and exposure to the forearms. The skin surface area would increase to 2,600 cm <sup>2</sup> (Popendorf 1982). | Exposure would range from 1.0 to 2.0 times the exposure level. |
| Dermal exposure duration for the bleach plant operator                             | The duration of the exposure was assumed to be 2 hours since the operator spends approximately 75% of the shift in the control room (NIOSH 1983). The durations are the maximum since the operators were assumed to be exposed for all the time they spend outside the control room. | Reasonable range in the duration would be 0.8 to 2 hours since the operator spends 75 to 90% of the shift in the control room.  | Exposure would range from 0.4 to 1.0 times the exposure level. |

(continued)

TABLE 3-8 (continued)

| Uncertainty                                   | Associated assumption   | Reasonable possible variance of assumption              | Effects on results   |
|---|---|---|--|
| Dermal exposure duration for pulp testers     | The duration of the exposure was assumed to be 6 hours since the operator spends 25% of the shift in the control room (NIOSH 1983). The durations are the maximum since the operators were assumed to be exposed 100% of the time outside the control room.               | Reasonable range in the duration would be 4 to 8 hours. | Exposure would range from 0.7 to 1.4 times the exposure level. |
| Dermal exposure duration for utility operator | The duration of the exposure was assumed to be 6 hours since the operator spends approximately 20% of the shift in the control room (NIOSH 1983). The durations are the maximum since the operators were assumed to be exposed 100% of the time outside the control room. | Reasonable range in the duration would be 4 to 8 hours. | Exposure would range from 0.7 to 1.4 times the exposure level. |

remain constant throughout the drying phase. The partial pressure of 2378 TCDD and 2378 TCDF are calculated using Equation 6. The ideal gas law equation is presented in Equation 14. This equation transforms into Equation 15 by solving the right-hand side of the equation for moles per volume ( $m^3$ ) and then multiplying both sides of the equation by the molecular weight to obtain the inhalation exposure concentration of 2378 TCDD/2378 TCDF.

$$P \times V = n \times R \times T \quad \text{Equation 14}$$

$$C_m = M \times \frac{n}{V} = M \times \frac{P}{RT} \times 1 \times 10^6 \quad \text{Equation 15}$$

where:  $P$  = partial pressure of 2378 TCDD/2378 TCDF, atm  
 $V$  = volume of the gas,  $m^3$   
 $n$  = number of moles, moles  
 $R$  = ideal gas constant, atm. liter/mole.K (0.0821)  
 $T$  = temperature of the gas, K  
 $C_m$  = concentration of 2378 TCDD/2378 TCDF in the vapor,  $mg/m^3$   
 $M$  = molecular weight, g/mole

The inhalation exposure concentration in  $mg/m^3$  based on the ideal gas law is then substituted into Equation 9 resulting in a daily inhalation exposure ( $I_v$ ) in  $mg/day$ . Table 3-9 summarizes the variables used to calculate inhalation exposure levels for pulp-drying and utility operators from volatilization from wet pulp and presents exposure estimates.

The relative toxicity of 2378 TCDF with respect to 2378 TCDD can be determined by calculating TEQ values. The percent exposure due to 2378 TCDD can also be calculated. Using Equations 10 and 11, these two variables are calculated. Table 3-10 presents the daily and lifetime average daily TEQ and percent exposure due to 2378 TCDD from volatilization from wet pulp for pulp-drying operators. Table 3-11 presents the assumptions and uncertainties in the variables used to calculate the daily exposure for the pulp-drying operators from volatilization.

TABLE 3-9. ESTIMATED INHALATION EXPOSURE TO 2378 TCDD and 2378 TCDF  
FOR PULP DRYING WORKERS FROM VOLATILIZATION

| Variable  | 2378 TCDD             |                       | 2378 TCDF             |                       | Reference                     |
|---|-----------------------|-----------------------|-----------------------|-----------------------|-------------------------------|
|   | Low                   | High                  | Low                   | High                  |                               |
| Vapor pressure, atm (P°) @ 71°C   | $1.6 \times 10^{-9}$  | $1.6 \times 10^{-9}$  | $2.0 \times 10^{-6}$  | $2.0 \times 10^{-6}$  | Schroy 1984, See Table 3-11   |
| Weight fraction of 2378 TCDD/2378 TCDF in the wet pulp, dry basis         | $0.1 \times 10^{-12}$ | $4.9 \times 10^{-11}$ | $2.5 \times 10^{-13}$ | $2.62 \times 10^{-9}$ | Table 2-5 104-Mill Study data |
| Mole fraction of 2378 TCDD/2378 TCDF (Xa), wet basis                      | $7.0 \times 10^{-16}$ | $3.4 \times 10^{-13}$ | $1.8 \times 10^{-15}$ | $1.8 \times 10^{-11}$ | See Table 3-5                 |
| Partial pressure of 2378 TCDD/2378 TCDF, atm (P)                          | $1.1 \times 10^{-24}$ | $5.5 \times 10^{-22}$ | $3.5 \times 10^{-21}$ | $3.7 \times 10^{-17}$ | Calculated                    |
| Molecular weight, g/g-mole (M)  | 322                   | 322                   | 306                   | 306                   | EPA 1989b                     |
| Ideal gas constant, atm liter/g-mole °K                                   | 0.0821                | 0.0821                | 0.0821                | 0.0821                | Felder 1978                   |
| Temperature, °K (T)   | 298                   | 298                   | 298                   | 298                   | See Table 3-11                |
| Concentration of 2378 TCDD/2378 TCDF in the vapor, mg/m <sup>3</sup> (Cm) | $1.5 \times 10^{-17}$ | $7.2 \times 10^{-15}$ | $4.4 \times 10^{-14}$ | $4.6 \times 10^{-10}$ | Calculated                    |
| Exposure duration, h/day (ED)   |                       |                       |                       |                       |                               |
| - Pulp-drying operators   | 2                     | 2                     | 2                     | 2                     | See Table 3-11                |
| - Utility operators   | 2                     | 2                     | 2                     | 2                     | See Table 3-11                |
| Daily inhalation, mg/day (Iv)   |                       |                       |                       |                       |                               |
| - Pulp-drying operators   | $3.7 \times 10^{-17}$ | $1.8 \times 10^{-14}$ | $1.1 \times 10^{-13}$ | $1.1 \times 10^{-9}$  | Calculated                    |
| - Utility operators   | $3.7 \times 10^{-17}$ | $1.8 \times 10^{-14}$ | $1.1 \times 10^{-13}$ | $1.1 \times 10^{-9}$  | Calculated                    |

TABLE 3-10. ESTIMATED TOXICITY EQUIVALENTS AND PERCENT EXPOSURE DUE TO 2378 TCDD FOR PULP DRYING WORKERS FROM VOLATILIZATION

| Job category         | Daily TEQ, <sup>a</sup> mg/day  |                                  | Lifetime average daily TEQ, <sup>a</sup> mg/day-kg |                                  |
|----------------------|---------------------------------|----------------------------------|--|----------------------------------|
|                      | Low                             | High                             | Low  | High                             |
| Pulp-drying operator | $1.1 \times 10^{-14}$<br>(0.03) | $1.1 \times 10^{-10}$<br>(0.002) | $6.1 \times 10^{-17}$<br>(0.03)                    | $7.7 \times 10^{-13}$<br>(0.002) |
| Utility operator     | $1.1 \times 10^{-14}$<br>(0.03) | $1.1 \times 10^{-10}$<br>(0.002) | $6.1 \times 10^{-17}$<br>(0.03)                    | $7.7 \times 10^{-13}$<br>(0.002) |

<sup>a</sup> Values in parentheses are percent exposure to 2378 TCDD.



TABLE 3-11. ASSUMPTION AND UNCERTAINTIES IN ESTIMATING INHALATION EXPOSURE TO 2378 TCDD AND 2378 TCDF FOR PAPER MILL WORKERS FROM VOLATILIZATION

| Uncertainty   | Associated assumption  | Reasonable possible variance of assumption              | Effects on results   |
|---|--|---|--|
| Vapor pressure for 2378 TCDF at 71°C was not found in literature. | The vapor pressure for 2378 TCDD from 25 to 71°C increased from $9.7 \times 10^{-13}$ to $1.6 \times 10^{-9}$ atm. Using the same increase in vapor pressure as 2378 TCDD, the vapor pressure of 2378 TCDF from 25 to 71°C would increase from $1.2 \times 10^{-9}$ to $2.6 \times 10^{-6}$ atm. | -   | -  |
| Temperature that the pulp/paper drying occurs.                    | The temperature would be approximately 70°C (Grant 1989.)  | -   | -  |
| Temperature of the air which contains 2378 TCDD/2378 TCDF.        | The temperature would be approximately 25°C when the vapors would be inhaled by the worker.  | -   | -  |
| Inhalation exposure duration for pulp-drying operator.            | The duration of the exposure was assumed to be 2 hours, since the operator spends a majority of the shift away from the drying machine.  | Reasonable range in the duration would be 1 to 4 hours. | Exposure would range from 0.5 to 2 times the exposure level. |
| Inhalation exposure duration for pulp-drying utility operator.    | The duration of the exposure was assumed to be 2 hours since the operator spends majority of the shift away from the drying machine.   | Reasonable range in the duration would be 1 to 6 hours. | Exposure would range from 0.5 to 3 times the exposure level. |

The following is an example of the calculation procedure (Equations 6, 15, and 9) used for estimating levels of daily inhalation exposure for pulp mill drying operators potentially exposed to 2378 TCDD/2378 TCDF from volatilization of wet pulp.

Lower limit of 2378 TCDD inhalation exposure level from volatilization for pulp operators

$$\begin{aligned} P_a &= P_a^\circ \times X_a \\ &= 1.6 \times 10^{-9} \text{ atm} \times 7.0 \times 10^{-16} \text{ (at } 71^\circ\text{C)} \\ &= 1.1 \times 10^{-24} \text{ atm} \end{aligned}$$

$$\begin{aligned} C_m &= 322 \text{ g/g-mole} \times \frac{1.1 \times 10^{-24} \text{ atm}}{0.0821 \frac{\text{atm liter}}{\text{g-mole K}^\circ} \times 298 \text{ K}} \times 1000 \text{ liter/m}^3 \times 1000 \text{ mg/g} \\ &= 1.5 \times 10^{-17} \text{ mg/m}^3 \end{aligned}$$

$$\begin{aligned} I_v &= 1.5 \times 10^{-17} \text{ mg/m}^3 \times 1.25 \text{ m}^3/\text{h} \times 2 \text{ h/day} \\ &= 3.7 \times 10^{-17} \text{ mg/day} \end{aligned}$$

Pulp dust may be generated during the pulp-drying and -handling operations, but actual dust concentration levels have not been measured (McCubbin 1989).

### 3.1.2.2 Level of Dermal Exposure--

Workers in the pulp-drying operations are potentially exposed to PCDDs and PCDFs through dermal contact with the wet or dry pulp. Dermal exposure may occur during pulp sheet weighing when sheets are added or removed by hand to achieve a predetermined weight. Fork-truck drivers usually do not handle the dry pulp. Dermal exposure to the wet or dry pulp is possible for the utility workers if personal protective equipment is not worn.

Dermal exposures to PCDDs and PCDFs were based on the worst-case assumption that pulp-drying workers do not wear any type of gloves that effectively limits exposure to PCDDs and PCDFs. Pulp-drying operators are potentially exposed to PCDDs and PCDFs while handling the dry pulp sheets during weighing

operations. This is similar to the handling of dry paper; therefore, the equation for handling paper was selected for the pulp-drying workers. Dermal exposure from handling dry paper or pulp is presented in Equation 16 (CPSC 1989).

$$\text{DED (mg/day)} = \frac{\text{DC (ppt)} \times \text{PW (g)}}{\text{ED (h/day)}} \div \text{PS (cm}^2\text{)} \times \text{R (h}^{-1}\text{)} \times \% \text{AD} \times \text{S (cm}^2\text{)} \times \text{Equation 16}$$

where DED = dermal exposure from handling dry material, mg/day  
 DC = 2378 TCDD/2378 TCDF concentration in the dry pulp, ppt  
 PW = weight of the dry pulp sheets, g  
 PS = surface area of the dry pulp sheets, cm<sup>2</sup>  
 R = rate of transfer from pulp to the skin, h<sup>-1</sup>  
 %AD = percent 2378 TCDD/2378 TCDF available for dermal absorption; fractional value used in calculations  
 S = skin surface area, cm<sup>2</sup>  
 ED = exposure duration, h/day

Dermal exposure duration was based on engineering judgment. It was assumed that only the palms and fingers of both hands of the pulp drying operator are in contact with the dry pulp sheets. Table 3-12 summarizes the variables and results for dermal exposure for the pulp-drying operator.

The following is an example of the calculation procedure used for estimating levels of dermal exposure for the pulp-drying operator potentially exposed to TCDDs and TCDFs in the handling of dry pulp; the lower limit of exposure to 2378 TCDD is used in the example:

$$\begin{aligned} \text{DED} &= 0.1 \times 10^{-12} \frac{\text{g}}{\text{g}} \times 454 \text{ g/6000 cm}^2 \times 0.0005 \text{ h}^{-1} \times 0.25 \times 250 \text{ cm}^2 \times 2 \text{ h/day} \\ &\quad \times 1000 \text{ mg/g} \\ &= 4.7 \times 10^{-13} \text{ mg/day} \end{aligned}$$

Utility workers who handle the wet and dry pulp during cleanup of the production area were assumed to come into contact with the pulp 2 hours per day. The worst-case assumption that the workers do not wear any type of glove that effectively limits exposure to PCDDs and PCDFs was also used in

TABLE 3-12. ESTIMATED DERMAL EXPOSURE TO 2378 TCDD AND 2378 TCDF  
FOR PULP DRYING OPERATORS

| Variable   | 2378 TCDD             |                       | 2378 TCDF             |                      | Reference      |
|--|-----------------------|-----------------------|-----------------------|----------------------|----------------|
|  | Low                   | High                  | Low                   | High                 |                |
| 2378 TCDD/2378 TCDF concentration in the dry pulp, dry basis, ppt (DC)     | 0.1                   | 49                    | 0.25                  | 2,620                | See Table 2-5  |
| Weight of the dry pulp sheets, g (PW)                                      | 454                   | 454                   | 454                   | 454                  | See Table 3-15 |
| Surface area of the dry pulp sheets, cm <sup>2</sup> (PS)                  | 6,000                 | 6,000                 | 6,000                 | 6,000                | See Table 3-15 |
| Rate of transfer from the pulp to the skin, h <sup>-1</sup> (R)            | 0.0005                | 0.0005                | 0.0005                | 0.0005               | EPA 1989c      |
| Percent 2378 TCDD/2378 TCDF available for dermal absorption, percent (%AD) | 25                    | 25                    | 25                    | 25                   | EPA 1989c      |
| Skin surface area, cm <sup>2</sup>   | 250                   | 300                   | 250                   | 300                  | See Table 3-15 |
| Exposure duration, h/day (ED)  | 2                     | 2                     | 2                     | 2                    | See Table 3-15 |
| Dermal exposure, mg/day (DED)  | 4.7x10 <sup>-13</sup> | 2.8x10 <sup>-10</sup> | 1.2x10 <sup>-12</sup> | 1.5x10 <sup>-8</sup> | Calculated     |

this exposure assessment. The equation for handling wet pulp was selected for this operation since the workers have a higher potential for contacting wet pulp rather than dry pulp. This equation was presented previously in Equation 12. The 2378 TCDD and 2378 TCDF concentrations for pulp from Table 2-5 are reported on a dry basis. Since the utility workers are handling wet pulp, this concentration was adjusted to a wet basis by adjusting for the estimated average pulp composition (11 percent) and assuming that only the aqueous phase contains 2378 TCDD/2378 TCDF and water. This corresponds to multiplying the 2378 TCDD/2378 TCDF weight fractions on a dry basis by 0.12 to obtain weight fractions on a wet basis. Table 3-13 summarizes the variables and results for dermal exposure for the pulp drying operator and the utility pulp drying operator.

Equations 10 and 11 are used to calculate the TEQ and the percent exposure due to 2378 TCDD. In these two equations, the daily inhalation exposure from volatilization (Iv) is replaced with the daily dermal exposure (DEW or DED) from 2378 TCDD and 2378 TCDF. Table 3-14 presents daily and lifetime average daily TEQ and percent exposure due to 2378 TCDD from dermal exposure to wet and dry pulp for workers in the pulp-drying operations. Table 3-15 presents the assumptions and uncertainties in the variables used to calculate dermal exposures for workers in the pulp drying operations.

### 3.1.3 Papermaking

Papermaking operations include wet-end additives/stock preparations, coating preparation, paper machine wet-end, paper machine dry-end, and off-machine coating. There is potential for pulp exposure in the papermaking stage of pulp and papermaking operations. In this stage, bleached pulp containing PCDDs and PCDFs is processed, and it is assumed that the concentrations of PCDDs and PCDFs remain constant. PCDDs and PCDFs can also be introduced into this stage by the use of recycled white water from the paper

TABLE 3-13. ESTIMATED DERMAL EXPOSURE TO 2378 TCDD AND 2378 TCDF  
FOR PULP DRYING UTILITY OPERATORS

| Variable  | 2378 TCDD             |                       | 2378 TCDF             |                       | Reference      |
|---|-----------------------|-----------------------|-----------------------|-----------------------|----------------|
|   | Low                   | High                  | Low                   | High                  |                |
| 2378 TCDD/2378 TCDF concentration, wet basis, ppt (DC)  | 0.012                 | 5.88                  | 0.03                  | 314                   | See Table 3-8  |
| Density of the wet pulp, mg/cm <sup>3</sup> ( $\rho$ )  | 1,000                 | 1,000                 | 1,000                 | 1,000                 | See Table 3-8  |
| Liquid film thickness of the wet pulp, cm (FT)  | 0.025                 | 0.025                 | 0.025                 | 0.025                 | See Table 3-8  |
| Liquid equilibrium partition coefficient of 2378 TCDD/2378 TCDF from water, dimensionless (K) | 13,000                | 13,000                | 29,000                | 29,000                | EPA 1989c      |
| Absorption coefficient of 2378 TCDD/2378 TCDF through the skin, h <sup>-1</sup> (AD)          | 0.012                 | 0.012                 | 0.012                 | 0.012                 | EPA 1989c      |
| Skin surface area, cm <sup>2</sup> (S)  | 250                   | 300                   | 250                   | 300                   | See Table 3-15 |
| Exposure duration, h/day (ED)   | 2                     | 2                     | 2                     | 2                     | See Table 3-15 |
| Dermal exposure, mg/day (DEW)   | $1.4 \times 10^{-16}$ | $8.1 \times 10^{-14}$ | $1.6 \times 10^{-16}$ | $2.0 \times 10^{-12}$ | Calculated     |

TABLE 3-14. ESTIMATED TOXICITY EQUIVALENTS AND PERCENT EXPOSURE DUE TO 2378 TCDD FOR PULP-DRYING OPERATIONS FROM DERMAL EXPOSURE

| Variable                     | Daily TEQ, mg/kg <sup>a</sup> |                              | Lifetime average daily TEQ, mg/day-kg |                              |
|------------------------------|-------------------------------|------------------------------|---------------------------------------|------------------------------|
|                              | Low                           | High                         | Low                                   | High                         |
| Pulp-drying operator         | $5.9 \times 10^{-13}$<br>(29) | $1.8 \times 10^{-9}$<br>(2)  | $3.3 \times 10^{-15}$<br>(29)         | $1.2 \times 10^{-11}$<br>(2) |
| Pulp-drying utility operator | $1.5 \times 10^{-16}$<br>(47) | $2.8 \times 10^{-13}$<br>(4) | $8.6 \times 10^{-19}$<br>(47)         | $1.9 \times 10^{-15}$<br>(4) |

<sup>a</sup> Value in parentheses are percent exposure to 2378 TCDD.

TABLE 3-15. ASSUMPTIONS AND UNCERTAINTIES IN ESTIMATING DERMAL EXPOSURE TO 2378 TCDD AND 2378 TCDF FOR PULP DRYING OPERATORS

| Uncertainty  | Associated assumption   | Reasonable possible variance of assumption  | Effects on results   |
|--|---|---|--|
| Weight of the dry pulp sheets.   | The dry pulp sheets weigh approximately 454 g (Sullivan 1989).  |   |  |
| Surface area of the dry pulp sheets.   | The surface area of the dry pulp sheets is 6,000 cm <sup>2</sup> (Sullivan 1989).   |   |  |
| Rate of transfer from the dry pulp to the skin.  | The transfer rate from paper to skin is 0.0005 (EPA 1989c). PEI assumed the transfer rate from paper to skin would be the same as transfer from dry pulp to skin.   |   |  |
| The skin surface area where the pulp drying operators and utility operators would be exposed to 2378 TCDD and 2378 TCDF. | The exposed skin surface area was estimated by PEI to be 100 percent of palm and finger surfaces of both hands. The high and low represent the difference between the surface area of men's and women's hands. The exposed skin surface area is 250 cm <sup>2</sup> for females and 300 cm <sup>2</sup> for males (NCASI 1988). | The exposed skin surface area could potentially include exposure to both hands (front and back). The skin surface area would increase to 1300 cm <sup>2</sup> (Popendorf 1982). | Exposure would range from 5 to 5.2 times the exposure level. |

(continued)



TABLE 3-15 (continued)

| Uncertainty  | Associated assumption   | Reasonable possible variance of assumption              | Effects on results   |
|--|---|---|--|
| Dermal exposure duration for pulp drying operators.    | The duration of the exposure was assumed by PEI to be 8 hours, since the worker will be in contact with the pulp during his job activities throughout the shift.  |   |  |
| Dermal exposure duration for drying utility operators. | The duration of the exposure was assumed by PEI to be 2 hours, since the operator will be in contact with the pulp for half the shift during cleanup and maintenance activities in the production area. | Reasonable range in the duration would be 1 to 8 hours. | Exposure would range from 0.5 to 4 times the exposure level. |

machine to dilute the pulp slurry prior to its feeding into the wet end of the papermaking machine. The additional PCDD/PCDF contribution, however, should be small in comparison to the concentrations of PCDDs and PCDFs in the bleached pulp. In the papermaking and finishing operations, a potential for PCDD and PCDF exposure through dermal absorption exists if workers come in contact with either dioxin/furan-contaminated wet pulp which is to be fed into beaters or refining equipment or with the paper products.

The workers in dry-end operations are potentially exposed to PCDDs and PCDFs through dermal contact with paper products, inhalation of vapors during drying operations, and inhalation of paper dust during normal process operations. For a particular plant evaluated in a NIOSH study, engineering controls and work practices used to prevent or decrease the amount of dust inhaled included exhaust systems, the use of dust masks, and cleaning of equipment every shift to remove accumulated paper dust. A NCASI study to determine the particulate size distribution of paper dust showed that total paper dust mass concentration levels ranged from 0.2 to 4.90 mg/m<sup>3</sup> during normal operations, and 31 to 109 mg/m<sup>3</sup> at the time of operation during blow-down (operations requiring approximately 15 minutes per shift for machinery cleaning) (NCASI 1988a). Table 3-16 presents the particulate size distribution results from the NCASI study. In the NIOSH study, both general ventilation and local ventilation (Torit Dust Collection Systems) were provided in one of the eighteen plants studied; dilution ventilation rates were reported to be 6 to 10 air changes per hour. The number of air changes was not used to calculate the ventilation rate.

TABLE 3-16. PARTICULATE SIZE DISTRIBUTION BY TOTAL DUST CONCENTRATION<sup>a</sup>

| Mass concentration range |         | Concentration, mg/m <sup>3</sup> |                 |             |        |
|--------------------------|---------|----------------------------------|-----------------|-------------|--------|
|                          |         | <2 $\mu$ m                       | 1 to 10 $\mu$ m | >10 $\mu$ m | Total  |
| Low                      | Average | 0.12                             | 0.08            | 0.09        | 0.28   |
|                          | Minimum | 0.07                             | 0.00            | 0.05        | 0.21   |
|                          | Maximum | 0.16                             | 0.20            | 0.18        | 0.46   |
| Medium                   | Average | 0.31                             | 0.32            | 0.41        | 1.04   |
|                          | Minimum | 0.00                             | 0.11            | 0.16        | 0.77   |
|                          | Maximum | 1.05                             | 0.70            | 0.66        | 1.51   |
| High                     | Average | 0.09                             | 0.60            | 3.04        | 3.73   |
|                          | Minimum | 0.00                             | 0.19            | 2.30        | 2.97   |
|                          | Maximum | 0.24                             | 1.00            | 3.73        | 4.90   |
| Blowdown                 | Average | 0.30                             | 4.76            | 62.78       | 67.84  |
|                          | Minimum | 0.00                             | 2.12            | 25.56       | 30.93  |
|                          | Maximum | 0.56                             | 7.35            | 101.69      | 109.03 |

<sup>a</sup> (NCASI 1988a)

## 3.1.3.1 Level of Inhalation Exposure--

Three job categories of workers in the paper mill (i.e., wet-end operator, dry-end operator, and utility operator) are potentially exposed to PCDDs and PCDFs.

There are two routes for inhalation exposure: 1) vapors from volatilization of PCDDs and PCDFs, and 2) particulates (dust). The utility operator and dry-end operator may be exposed by both routes of inhalation exposure, while the wet-end operator is estimated to be exposed only from volatilization of PCDDs and PCDFs. It was estimated that wet-end operators, dry-end operators, and utility operators spend 2, 4, and 6 hours of their shifts, respectively, in areas of the plant in which there is a potential for inhalation exposure.

Volatilization--The same calculation procedures previously employed to estimate inhalation exposure to PCDDs and PCDFs by vaporization (using Equations 6, 15, and 9) for pulp drying workers was used to estimate inhalation

exposure to paper mill workers. Table 3-17 summarizes the variables used to calculate inhalation exposure for the paper mill workers to volatilization of PCDDs and PCDFs and presents exposure estimates.

The relative toxicity of 2378 TCDF with respect to 2378 TCDD can be determined by calculating TEQ. In addition, the percent exposure due to 2378 TCDD can also be calculated. Using Equations 10 and 11, these two variables are calculated. Table 3-18 presents the daily and lifetime average daily TEQ and percent exposure due to 2378 TCDD for paper mill workers from volatilization from wet pulp. Table 3-19 presents the assumptions and uncertainties in the variables used to calculate the daily exposure and lifetime average daily exposure for paper mill workers from volatilization from wet pulp.

Particulate matter--Equation 17 was used to calculate the inhalation exposure from PCDD and PCDF contained in particulate matter generated during paper mill operations. This equation is similar to Equation 9 except that the  $C_m$  in this equation is for the total particulate concentration rather than the 2378 TCDD/2378 TCDF concentration. In the absence of data on 2378 TCDD/2378 TCDF concentrations in the paper dust, the fraction of 2378 TCDD/2378 TCDF in the dry pulp was used to allocate the portion of the paper dust which is 2378 TCDD/2378 TCDF. The dry weight fraction of 2378 TCDD/2378 TCDF in the pulp, as reported in the 104-Mill Study, was used in the calculation because the paper dust that is emitted is dry.

$$I_p = C_m \text{ (mg/m}^3\text{)} \times 1.25 \text{ m}^3\text{/h} \times \text{ED (h/day)} \times W \quad \text{Equation 17}$$

where  $I_p$  = daily inhalation of particulate matter, mg/day

$C_m$  = concentration of paper mill dust, mg/m<sup>3</sup> (with existing engineering controls)

TABLE 3-17. ESTIMATED INHALATION EXPOSURE TO 2378 TCDD and 2378 TCDF  
FOR PAPER MILL WORKERS FROM VOLATILIZATION

| Variable  | 2378 TCDD             |                       | 2378 TCDF             |                       | Reference                     |
|---|-----------------------|-----------------------|-----------------------|-----------------------|-------------------------------|
|   | Low                   | High                  | Low                   | High                  |                               |
| Weight fraction of 2378 TCDD/2378 TCDF in the dry pulp, dry basis | $0.1 \times 10^{-12}$ | $4.9 \times 10^{-11}$ | $2.5 \times 10^{-13}$ | $2.62 \times 10^{-9}$ | Table 2-5 104-Mill Study data |
| Mole fraction of 2378 TCDD/2378 TCDF in the pulp, wet basis (Xa)  | $7.0 \times 10^{-16}$ | $3.4 \times 10^{-13}$ | $1.8 \times 10^{-15}$ | $1.8 \times 10^{-11}$ | See Table 3-5                 |
| Vapor pressure, atm (P°) @ 71°C                                   | $1.6 \times 10^{-9}$  | $1.6 \times 10^{-9}$  | $2.0 \times 10^{-6}$  | $2.0 \times 10^{-6}$  | Schroy 1984, See Table 3-11   |
| Molecular weight, g/g-mole (M)                                    | 322                   | 322                   | 306                   | 306                   | EPA 1989b                     |
| Temperature, °K (T)   | 298                   | 298                   | 298                   | 298                   | See Table 3-11                |
| Concentration of 2378 TCDD/2378 TCDF in the vapor, ppm (Cv)       | $1.5 \times 10^{-17}$ | $7.2 \times 10^{-15}$ | $4.4 \times 10^{-14}$ | $4.6 \times 10^{-10}$ | Calculated                    |
| Ideal gas constant, atm liter/g-mole °K                           | 0.0821                | 0.0821                | 0.0821                | 0.0821                | Felder 1978                   |
| Exposure duration, h/day (ED)                                     |                       |                       |                       |                       |                               |
| - Wet-end operators   | 2                     | 2                     | 2                     | 2                     | See Table 3-19                |
| - Dry-end operators   | 4                     | 4                     | 4                     | 4                     | See Table 3-19                |
| - Utility operators   | 6                     | 6                     | 6                     | 6                     | See Table 3-19                |
| Daily inhalation, mg/day (Iv)                                     |                       |                       |                       |                       |                               |
| - Wet-end operators   | $3.7 \times 10^{-17}$ | $1.8 \times 10^{-14}$ | $1.1 \times 10^{-13}$ | $1.1 \times 10^{-9}$  | Calculated                    |
| - Dry-end operators   | $7.4 \times 10^{-17}$ | $3.6 \times 10^{-14}$ | $2.2 \times 10^{-13}$ | $2.3 \times 10^{-9}$  | Calculated                    |
| - Utility operators   | $1.1 \times 10^{-16}$ | $5.4 \times 10^{-14}$ | $3.3 \times 10^{-13}$ | $3.4 \times 10^{-9}$  | Calculated                    |

TABLE 3-18. ESTIMATED TOXICITY EQUIVALENTS AND PERCENT EXPOSURE DUE TO 2378 TCDD FOR PAPER MILL WORKERS FROM VOLATILIZATION

| Job category     | Daily TEQ, <sup>a</sup> mg/day  |                                  | Lifetime average daily TEQ, <sup>a</sup> mg/day-kg |                                  |
|------------------|---------------------------------|----------------------------------|--|----------------------------------|
|                  | Low                             | High                             | Low  | High                             |
| Wet-end operator | $1.1 \times 10^{-14}$<br>(0.03) | $1.1 \times 10^{-10}$<br>(0.002) | $6.1 \times 10^{-17}$<br>(0.03)                    | $7.7 \times 10^{-13}$<br>(0.002) |
| Dry-end operator | $2.2 \times 10^{-14}$<br>(0.03) | $2.3 \times 10^{-10}$<br>(0.002) | $1.2 \times 10^{-16}$<br>(0.03)                    | $1.5 \times 10^{-12}$<br>(0.002) |
| Utility operator | $3.3 \times 10^{-14}$<br>(0.03) | $3.4 \times 10^{-10}$<br>(0.002) | $1.8 \times 10^{-16}$<br>(0.03)                    | $2.3 \times 10^{-12}$<br>(0.002) |

<sup>a</sup> Values in parentheses are percent exposure to 2378 TCDD.

TABLE 3-19. ASSUMPTION AND UNCERTAINTIES IN ESTIMATING INHALATION EXPOSURE TO 2378 TCDD AND 2378 TCDF FOR PAPER MILL WORKERS FROM VOLATILIZATION

| Uncertainty  | Associated assumption  | Reasonable possible variance of assumption              | Effects on results   |
|--|--|---|--|
| The amount of 2378 TCDD/2378 TCDF in the paper dust. | The fraction of 2378 TCDD/2378 TCDF in the paper dust was assumed to equal the dry weight fraction in the pulp.                        |   |  |
| Inhalation exposure duration for wet-end operator.   | The duration of the exposure was assumed to be 2 hours, since the operator spends a majority of the shift away from the paper machine. | Reasonable range in the duration would be 1 to 4 hours. | Exposure would range from 0.5 to 2 times the exposure level.   |
| Inhalation exposure duration for dry-end operator.   | The duration of the exposure was assumed to be 4 hours since the operator spends half of the shift away from the paper machine.        | Reasonable range in the duration would be 2 to 6 hours. | Exposure would range from 0.5 to 1.5 times the exposure level. |
| Inhalation exposure duration for utility operator.   | The duration of the exposure was assumed to be 6 hours, since the operator spends a majority of the shift near the paper machine.      | Reasonable range in the duration would be 4 to 8 hours. | Exposure would range from 0.7 to 1.3 times the exposure level. |

ED = exposure duration, h/day

W = weight fraction 2378 TCDD/2378 TCDF in the paper dust

Table 3-20 summarizes the variables used to calculate the exposure to workers from the particulate matter containing PCDDs and PCDFs generated during paper mill operations.

Equations 10 and 11 are used to calculate the TEQ and the percent exposure due to 2378 TCDD. In these two equations, the daily inhalation exposure from volatilization (TEQ<sub>v</sub>) for 2378 TCDD and 2378 TCDF are replaced with the daily inhalation exposure from particulate matter (TEQ<sub>p</sub>) for 2378 TCDD and 2378 TCDF. Table 3-21 presents the daily and lifetime average daily TEQ and percent exposure due to 2378 TCDD from dry particulate matter for paper mill workers. Table 3-22 presents the assumptions and uncertainties in the variables used to calculate the daily exposure for paper mill workers.

The following is an example of the calculation procedure (Equation 17) used for estimating levels of daily inhalation exposure for dry-end operators exposed to TCDD from particulate matter:

Lower limit for 2378 TCDD inhalation exposure levels from particulate matter for dry-end operators

$$\begin{aligned} I_p &= 0.21 \text{ mg/m}^3 \times 1.25 \text{ m}^3/\text{h} \times 4 \text{ h/day} \times 0.1 \times 10^{-12} \\ &= 1.0 \times 10^{-13} \text{ mg/day} \end{aligned}$$

The following is an example of the calculation procedure for estimating daily TEQ and percent daily exposure due to 2378 from particulate matter.

Lower limit for daily TEQ and percent daily exposure due to TCDD for dry-end loader operators from particulate matter

$$\begin{aligned} \text{DTEQ}_p &= 1.0 \times 10^{-13} + (0.1 \times 2.6 \times 10^{-13}) \\ &= 1.3 \times 10^{-13} \\ \% \text{TCDD}_p &= 1.0 \times 10^{-13} / (1.0 \times 10^{-13} + 2.6 \times 10^{-13}) \times 100 \\ &= 29\% \end{aligned}$$



TABLE 3-20. ESTIMATED INHALATION EXPOSURE TO 2378 TCDD AND 2378 TCDF  
FOR PAPER MILL OPERATORS FROM PARTICULATE MATTER

| Variable  | 2378 TCDD             |                       | 2378 TCDF             |                       | Reference  |
|---|-----------------------|-----------------------|-----------------------|-----------------------|------------|
|   | Low                   | High                  | Low                   | High                  |            |
| Concentration of paper mill dust, mg/m <sup>3</sup> (Cm) <sup>a</sup> |                       |                       |                       |                       |            |
| - Dry-end operator  | 0.21                  | 4.9                   | 0.21                  | 4.9                   | Table 3-16 |
| - Utility operator  | 31                    | 109                   | 31                    | 109                   | Table 3-16 |
| Amount of 2378 TCDD/-<br>2378 TCDF in the paper dust, dry basis (WF)  |                       |                       |                       |                       |            |
| - Dry-end operator  | 0.1x10 <sup>-12</sup> | 4.9x10 <sup>-11</sup> | 2.5x10 <sup>-13</sup> | 2.62x10 <sup>-9</sup> | Table 2-5  |
| - Utility operator  | 0.1x10 <sup>-12</sup> | 4.9x10 <sup>-11</sup> | 2.5x10 <sup>-13</sup> | 2.62x10 <sup>-9</sup> | Table 2-5  |
| Exposure duration, h/day (ED)   |                       |                       |                       |                       |            |
| - Dry-end operator  | 4                     | 4                     | 4                     | 4                     | Table 3-22 |
| - Utility operator  | 1                     | 1                     | 1                     | 1                     | Table 3-22 |
| Daily inhalation, mg/day (Ip)   |                       |                       |                       |                       |            |
| - Dry-end operator  | 1.0x10 <sup>-13</sup> | 1.2x10 <sup>-9</sup>  | 2.6x10 <sup>-13</sup> | 6.4x10 <sup>-8</sup>  | Calculated |
| - Utility operator  | 3.9x10 <sup>-12</sup> | 6.7x10 <sup>-9</sup>  | 9.7x10 <sup>-12</sup> | 3.6x10 <sup>-7</sup>  | Calculated |

<sup>a</sup> The high dust concentration reported for utility operators represent those achieved during blowdown operations over a short time period and do not represent a violation of the 8-hour OSHA PEL of 15 mg/m<sup>3</sup> for nuisance dust.

TABLE 3-21. ESTIMATED TOXICITY EQUIVALENTS AND PERCENT EXPOSURE DUE TO 2378 TCDD FOR PAPER MILL OPERATORS FROM PARTICULATE MATTER

| Job category     | Daily TEQ, <sup>a</sup> mg/day |                             | Lifetime average daily TEQ, <sup>a</sup> mg/day-kg |                              |
|------------------|--------------------------------|-----------------------------|--|------------------------------|
|                  | Low                            | High                        | Low  | High                         |
| Dry-end operator | $1.3 \times 10^{-13}$<br>(29)  | $7.6 \times 10^{-9}$<br>(2) | $7.3 \times 10^{-16}$<br>(29)                      | $5.1 \times 10^{-11}$<br>(2) |
| Utility operator | $4.8 \times 10^{-12}$<br>(29)  | $4.2 \times 10^{-8}$<br>(2) | $2.7 \times 10^{-14}$<br>(29)                      | $2.9 \times 10^{-10}$<br>(2) |

<sup>a</sup> Values in parentheses are percent exposure to 2378 TCDD.

TABLE 3-22. ASSUMPTION AND UNCERTAINTIES IN ESTIMATING INHALATION EXPOSURE TO 2378 TCDD AND 2378 TCDF FOR PAPER MILL WORKERS FROM PARTICULATE MATTER

| Uncertainty  | Associated assumption  | Reasonable possible variance of assumption                  | Effects on results   |
|--|--|---|--|
| Inhalation exposure duration for dry-end operator. | The duration of the exposure was assumed to be 4 hours, since the operator spends half of the shift in operations which generates dust.  | Reasonable range in the duration would be 2 to 8 hours.     | Exposure would range from 0.5 to 2 times the exposure level.   |
| Inhalation exposure duration for utility operator. | The duration of the exposure was assumed to be 1 hour. The operator would be exposed to paper dust during blowdown and for a period of time after blowdown for the dust to settle. | Reasonable range in the duration would be 0.5 to 1.5 hours. | Exposure would range from 0.5 to 1.5 times the exposure level. |

### 3.1.3.2 Level of Dermal Exposure--

Dermal exposure levels to 2378 TCDD and 2378 TCDF were computed based on the worst-case assumption that workers do not wear any type of gloves that effectively limit exposure to PCDDs and PCDFs. The same calculation procedures previously employed to estimate dermal exposure levels for the pulp mill operators and pulp-drying workers were used to estimate the dermal exposure levels for the paper mill operators.

The wet-end operator responsibilities include pulping, bleaching, beating, refining, application of additives, and blending proportioning. Dermal exposure duration was based on engineering judgment. The equation for handling wet material was selected for this operation, since the worker will be handling the wet end of the process line. This equation was presented in Equation 13. Table 3-23 summarizes the variables and results for dermal exposure for the paper mill wet-end operators.

The dry-end operator responsibilities include supercalendering, rewinding, slitting, cutting and sheeting, trimming, packaging, and shipping. Some shipping and packaging operations may be performed in a separate part of the same plant. Dermal exposure duration was based on engineering judgment. The equation for handling dry material was selected for this operation, since the worker handles dry paper. This equation was presented in Equation 17.

The utility operator responsibilities include machine cleaning (blow-down), and assisting dry-end and wet-end operators. Dermal exposure duration was based on engineering judgment. The equation for handling dry material was selected for this operation, since the worker has a higher potential for contacting dry paper than wet paper. This equation was presented in Equation 13. Table 3-24 presents the estimated dermal exposure to 2378 TCDD and 2378 TCDF for dry-end and utility operators.

TABLE 3-23. ESTIMATED DERMAL EXPOSURE TO 2378 TCDD AND 2378 TCDF  
FOR WET-END OPERATORS IN PAPER MILLS

| Variable  | 2378 TCDD             |                       | 2378 TCDF             |                       | Reference      |
|---|-----------------------|-----------------------|-----------------------|-----------------------|----------------|
|   | Low                   | High                  | Low                   | High                  |                |
| 2378 TCDD/2378 TCDF concentration, wet basis, ppt (DC)  | 0.012                 | 5.88                  | 0.03                  | 314                   | See Table 3-8  |
| Density of the wet pulp, mg/cm <sup>3</sup> ( $\rho$ )  | 1,000                 | 1,000                 | 1,000                 | 1,000                 | See Table 3-8  |
| Liquid film thickness of the pulp, cm (FT)  | 0.025                 | 0.025                 | 0.025                 | 0.025                 | See Table 3-8  |
| Liquid equilibrium partition coefficient of 2378 TCDD/-2378 TCDF from water deminsionless (K) | 13,000                | 13,000                | 29,000                | 29,000                | EPA 1989c      |
| Absorption coefficient of 2378 TCDD/-2378 TCDF through the skin h <sup>-1</sup> (AD)          | 0.012                 | 0.012                 | 0.012                 | 0.012                 | EPA 1989c      |
| Skin surface area, cm <sup>2</sup> (S)  | 250                   | 300                   | 250                   | 300                   | See Table 3-23 |
| Exposure duration, h/day (ED)   | 2                     | 2                     | 2                     | 2                     | See Table 3-23 |
| Dermal exposure, mg/day (DEW)   | $1.4 \times 10^{-16}$ | $8.1 \times 10^{-14}$ | $1.6 \times 10^{-16}$ | $2.0 \times 10^{-12}$ | Calculated     |

TABLE 3-24. ESTIMATED DERMAL EXPOSURE TO 2378 TCDD AND 2378 TCDF  
FOR PAPER MILL DRY-END OPERATORS AND UTILITY OPERATORS

| Variable   | 2378 TCDD             |                       | 2378 TCDF             |                      | Reference   |
|--|-----------------------|-----------------------|-----------------------|----------------------|-------------|
|  | Low                   | High                  | Low                   | High                 |             |
| 2378 TCDD/2378 TCDF concentration in the dry paper, dry basis, ppt (DC)    | 0.1                   | 49                    | 0.25                  | 2,620                | Table 2-5   |
| Weight of the dry paper, g (PW)  | 4.5                   | 4.5                   | 4.5                   | 4.5                  | NCASI 1988c |
| Surface area of the dry paper, cm <sup>2</sup> (PS)                        | 600                   | 600                   | 600                   | 600                  | NCASI 1988c |
| Rate of transfer from the paper to the skin, h <sup>-1</sup> (R)           | 0.0005                | 0.0005                | 0.0005                | 0.0005               | EPA 1989c   |
| Percent 2378 TCDD/2378 TCDF available for dermal absorption, percent (%AD) | 25                    | 25                    | 25                    | 25                   | EPA 1989c   |
| Skin surface area, cm <sup>2</sup> (S)                                     |                       |                       |                       |                      |             |
| - Dry-end operator   | 250                   | 300                   | 250                   | 300                  | Table 3-26  |
| - Utility operator   | 250                   | 300                   | 250                   | 300                  | Table 3-26  |
| Exposure duration, h/day (ED)  |                       |                       |                       |                      |             |
| - Dry-end operator   | 4                     | 4                     | 4                     | 4                    | Table 3-26  |
| - Utility operator   | 6                     | 6                     | 6                     | 6                    | Table 3-26  |
| Dermal, exposure mg/day (DED)  |                       |                       |                       |                      |             |
| - Dry-end operator   | $9.4 \times 10^{-14}$ | $5.5 \times 10^{-11}$ | $2.3 \times 10^{-13}$ | $2.9 \times 10^{-9}$ | Calculated  |
| - Utility operator   | $1.4 \times 10^{-13}$ | $8.3 \times 10^{-11}$ | $3.5 \times 10^{-13}$ | $4.4 \times 10^{-9}$ | Calculated  |

Equations 10 and 11 are used to calculate TEQ and percent exposure to 2378 TCDD. Table 3-25 presents daily and lifetime average daily TEQ and percent exposure due to 2378 TCDD for dermal exposure for workers in the papermill operations. Table 3-26 presents the assumptions and uncertainties in the variables used to calculate dermal exposures for paper mill workers. This includes the variables used to calculate dermal exposure from handling wet paper from Table 3-23 and handling dry paper from Table 3-24.

#### 3.1.4 Paper Converting

There is potential for PCDD and PCDF exposure in converting operations. The potential for dermal exposure arises from manual handling of dry bleached paper-based stock and finished product which contain PCDDs and PCDFs, whereas the potential for inhalation exposure arises from dry paper dusts created during the various converting operations. In the finishing stages, dermal contact may occur through arm and other skin surfaces during the following building operations: 1) building of the reel; 2) changing of the roll; and 3) trimming, cutting, transporting, wrapping, or packaging of the paper. For certain activities during converting operations (e.g., quality assurance), workers may also have skin contact with the final paper product.

Table 3-27 presents data from a NIOSH study of worker exposures to paper dust from the dry end of paper machines producing tissue paper, paper towels, and newsprint. The following is an estimation of inhalation exposure to 2378 TCDD and 2378 TCDF for pulp mill workers.

##### 3.1.4.1 Level of Inhalation Exposure--

The various job categories in the converting operation include machine operators; 3rd, 4th, and 5th hands; back tenders; slitters; and cutters. In

TABLE 3-25. ESTIMATED TOXICITY EQUIVALENTS AND PERCENT EXPOSURE DUE TO 2378 TCDD FOR PAPER MILL OPERATORS FROM DERMAL EXPOSURE

| Job category     | Daily TEQ, <sup>a</sup> mg/day |                              | Lifetime average daily TEQ, <sup>a</sup> mg/day-kg |                              |
|------------------|--------------------------------|------------------------------|--|------------------------------|
|                  | Low                            | High                         | Low  | High                         |
| Wet-end operator | $1.5 \times 10^{-16}$<br>(47)  | $2.8 \times 10^{-13}$<br>(4) | $8.6 \times 10^{-19}$<br>(47)                      | $1.9 \times 10^{-15}$<br>(4) |
| Dry-end operator | $1.2 \times 10^{-13}$<br>(29)  | $3.5 \times 10^{-10}$<br>(2) | $6.6 \times 10^{-16}$<br>(29)                      | $2.4 \times 10^{-12}$<br>(2) |
| Utility operator | $1.8 \times 10^{-13}$<br>(29)  | $5.2 \times 10^{-10}$<br>(2) | $9.8 \times 10^{-16}$<br>(29)                      | $3.5 \times 10^{-12}$<br>(2) |

<sup>a</sup> Values in parentheses are percent exposure to 2378 TCDD.

TABLE 3-26. ASSUMPTIONS AND UNCERTAINTIES IN ESTIMATING DERMAL EXPOSURE TO 2378 TCDD AND 2378 TCDF FOR PAPER MILL WORKERS

| Uncertainty   | Associated assumption  | Reasonable possible variance of assumption   | Effects on results   |
|---|--|--|--|
| The skin surface area where the wet-end, dry-end and utility operators would be exposed to 2378 TCDD and 2378 TCDF. | The exposed skin surface area was estimated by PEI to be 100% of palm and finger surfaces of both hands. The high and low represent the difference between the surface area of a men's and women's hands. The exposed skin surface is 250 cm <sup>2</sup> for females and 300 cm <sup>2</sup> for males (NCASI 1988c). | The exposed skin surface area could potentially include exposure to both hands (front and back). The skin surface area would increase to 1,300 cm <sup>2</sup> (Popendorf 1982). | Exposure would range from 5 to 5.2 times the exposure level. |
| Dermal exposure duration for the wet-end operator.  | The duration of the exposure was assumed to be 2 hours since the operator spends the majority of the shift away from the process area.   | Reasonable range in the duration would be 1 to 4 hours.  | Exposure would range from 0.5 to 2 times the exposure level. |
| Dermal exposure duration for the dry-end operator.  | The duration of the exposure was assumed to be 4 hours since the operator spends half of the shift in the process area.  | Reasonable range in the duration would be 2 to 8 hours.  | Exposure would range from 0.5 to 2 times the exposure level. |

(continued)



TABLE 3-26 (continued)

| Uncertainty                                    | Associated assumption   | Reasonable possible variance of assumption              | Effects on results   |
|--|---|---|--|
| Dermal exposure duration for utility operator. | The duration of the exposure was assumed to be 6 hours since the operator spends a majority of the shift in the process area. | Reasonable range in the duration would be 4 to 8 hours. | Exposure would range between 0.7 and 1.4 times the exposure level. |

TABLE 3-27. PERSONAL MONITORING RESULTS FOR  
EXPOSURE TO DUSTS IN PAPER CONVERTING OPERATIONS<sup>a</sup>

| Line  | Sample No. | Job classification | Total dust sampling time <sup>b</sup> (24-h) | Duration, min. | Concentration, mg/m <sup>3</sup> | Concentration, 8-h TWA, <sup>c</sup> mg/m <sup>3</sup> |
|---|------------|--------------------|--|----------------|----------------------------------|--|
| Paper Machine 1<br>(180-in. tissue machine)       | 1          | Third hand         | 0837-1533                                    | 416            | 9.1                              | 7.89   |
|   | 2          |                    | 1100-1124                                    | 24             | 10.0                             | 0.50   |
|   | 3          | Fourth hand        | 0857-1533                                    | 396            | 4.4                              | 3.6  |
|   | 4          |                    | 1100-1124                                    | 24             | 8.1                              | 0.4  |
|   | 5          |                    | 1622-2256                                    | 394            | 1.5                              | 1.2  |
|   | 6          |                    | 1533-2228                                    | 415            | 1.3                              | 1.1  |
|   | 7          | Fifth hand         | 1616-2256                                    | 400            | 0.9                              | 0.8  |
|   | 8          |                    | 1555-2238                                    | 403            | 0.7                              | 0.6  |
| Paper Machine 2<br>(180-in. tissue-towel machine) | 9          | Third hand         | 0835-1533                                    | 418            | 6.0                              | 5.2  |
|   | 10         |                    | 1618-2140                                    | 322            | 1.9                              | 1.3  |
|   | 11         |                    | 1605-2239                                    | 394            | 3.3                              | 2.7  |
|   | 12         | Fourth hand        | 0834-1533                                    | 419            | 1.5                              | 1.3  |
|   | 13         |                    | 1603-2241                                    | 398            | 9.1                              | 7.5  |
|   | 14         | Fifth hand         | 0834-1533                                    | 419            | 0.6                              | 0.52   |
|   |            |                    |  |                |                                  |  |
| Paper Machine 3<br>(258-in. news-print machine)   | 15         | Third hand         | 1630-2312                                    | 402            | 0.3                              | 0.20   |
|   | 16         | Fourth hand        | 1630-2300                                    | 390            | 1.0                              | 0.81   |
|   | 17         | Fifth hand         | 1628-2300                                    | 392            | 0.3                              | 0.25   |
|   | 18         | Core cutter        | 1631-2255                                    | 384            | 0.3                              | 0.20   |
|   | 19         | Back tender        | 1627-2258                                    | 391            | 0.3                              | 0.20   |
|   | 20         | Roll wrapper       | 1628-2256                                    | 388            | 0.4                              | 0.3  |

<sup>a</sup> (NIOSH 1983)

<sup>b</sup> Collected on pretared 5- $\mu$ m PVC filters and determined by gravitational analysis.

<sup>c</sup> The concentration data were recalculated for an 8-hour time-weighted average (TWA) for exposure modeling purposes.

the paper converting industry, dust generated during cutting and trimming operations is the only potential route for inhalation exposure. All operators in the production area were assumed to be exposed to the paper dust for the entire 8 hours of their shift.

The same calculation procedure previously employed to estimate inhalation exposure from dust for the paper mill operators was used to estimate the inhalation exposure levels from dust for the paper converting workers. Values for the dust concentration were calculated for an 8-hour exposure period from concentrations given in Table 3-27. Table 3-28 summarizes the variables and results used to calculate the exposure for the paper converting operator to dust containing 2378 TCDD and 2378 TCDF at the facility. The concentrations of 2378 TCDD and 2378 TCDF were obtained from Table 2-5. The concentrations were estimated to be the same in pulp as in paper assuming that PCDDs and PCDFs remain in the pulp through the papermaking and converting operations.

TABLE 3-28. ESTIMATED INHALATION EXPOSURE TO 2378 TCDD AND 2378 TCDF FOR PAPER CONVERTING WORKERS FROM PARTICULATE MATTER

| Variable  | 2378 TCDD             |                       | 2378 TCDF             |                       | Reference  |
|---|-----------------------|-----------------------|-----------------------|-----------------------|------------|
|   | Low                   | High                  | Low                   | High                  |            |
| Concentration of paper, mill dust, mg/m <sup>3</sup> (Cm) | 0.2                   | 7.9                   | 0.2                   | 7.9                   | Table 3-27 |
| Amount of dioxin in the mixture, (W)                      | $0.1 \times 10^{-12}$ | $4.9 \times 10^{-11}$ | $2.5 \times 10^{-13}$ | $2.62 \times 10^{-9}$ | Table 2-5  |
| Exposure duration, h/day (ED)                             | 8                     | 8                     | 8                     | 8                     | Table 3-30 |
| Daily inhalation, mg/day (Id)                             | $2.0 \times 10^{-13}$ | $3.9 \times 10^{-9}$  | $5.0 \times 10^{-13}$ | $2.1 \times 10^{-7}$  | Calculated |

Equations 10 and 11 are used to calculate the TEQ and the percent exposure due to 2378 TCDD. Table 3-29 presents the daily and lifetime average daily TEQ and percent exposure due to 2378 TCDD for the paper converting operators from particulate matter. Table 3-30 presents the assumptions and uncertainties in the variables used to calculate the daily exposure and lifetime average daily exposure for the paper converting operators from particulate matter.

#### 3.1.4.2 Level of Dermal Exposure--

Dermal exposure to 2378 TCDD and 2378 TCDF was based on the assumption that workers do not wear gloves that effectively limit exposure. The same calculation procedure as that used for the paper mill operators' dermal exposure was used to estimate the dermal exposure levels for the paper converting operator. Dermal exposure was based on engineering judgment. The equation for handling paper was selected for this operation since the worker will be handling dry paper rather than wet pulp. This equation was presented in Equation 17. Table 3-31 summarizes the variables and results for dermal exposure for the paper converting operators.

Equations 10 and 11 are used to calculate TEQ and the percent exposure due to 2378 TCDD. Table 3-32 presents the daily and lifetime average daily TEQ and percent exposure due to 2378 TCDD from dermal exposure for paper converting workers.

Table 3-33 presents the assumptions and uncertainties in the variables used to calculate the dermal exposures for paper converting workers in Table 3-31.

TABLE 3-29. ESTIMATED TOXICITY EQUIVALENTS AND PERCENT EXPOSURE DUE TO 2378 TCDD FOR PAPER CONVERTING OPERATORS FROM PARTICULATE MATTER

| Variable             | Daily TEQ, <sup>a</sup> mg/day |                             | Lifetime average daily TEQ, <sup>a</sup> mg/day-kg |                              |
|----------------------|--------------------------------|-----------------------------|--|------------------------------|
|                      | Low                            | High                        | Low  | High                         |
| Toxicity equivalents | $2.5 \times 10^{-13}$<br>(29)  | $2.5 \times 10^{-8}$<br>(2) | $1.4 \times 10^{-15}$<br>(29)                      | $1.7 \times 10^{-10}$<br>(2) |

<sup>a</sup> Values in parentheses are percent exposure to 2378 TCDD.

TABLE 3-30. ASSUMPTIONS AND UNCERTAINTIES IN ESTIMATING INHALATION EXPOSURE TO 2378 TCDD AND 2378 TCDF FOR PAPER CONVERTING WORKERS FROM PARTICULATE MATTER

| Uncertainty   | Associated assumption  | Reasonable possible variance of assumption | Effects on results |
|---|--|--|--------------------|
| Inhalation exposure duration for paper converting operator. | The duration of the exposure was assumed to be 8 hours since the operator is in the process area the entire shift. |  |                    |

TABLE 3-31. ESTIMATED DERMAL EXPOSURE TO 2378 TCDD AND 2378 TCDF  
FOR PAPER CONVERTING WORKERS

| Variable   | 2378 TCDD             |                       | 2378 TCDF             |                      | Reference   |
|--|-----------------------|-----------------------|-----------------------|----------------------|-------------|
|  | Low                   | High                  | Low                   | High                 |             |
| TCDD/TCDF concentration, ppt (DC)  | 0.1                   | 49                    | 0.25                  | 2,620                | Table 2-5   |
| Weight of the dry paper, g (PW)  | 4.5                   | 4.5                   | 4.5                   | 4.5                  | NCASI 1988c |
| Surface area of the dry paper, cm <sup>2</sup> (PS)                        | 600                   | 600                   | 600                   | 600                  | NCASI 1988c |
| Rate of transfer from the paper to the skin, h <sup>-1</sup> (R)           | 0.0005                | 0.0005                | 0.0005                | 0.0005               | EPA 1989c   |
| Percent 2378 TCDD/2378 TCDF available for dermal absorption percent (% AD) | 25                    | 25                    | 25                    | 25                   | EPA 1989c   |
| Skin surface area, cm <sup>2</sup> (S)                                     | 250                   | 300                   | 250                   | 300                  | Table 3-30  |
| Exposure duration, h/day (ED)  | 8                     | 8                     | 8                     | 8                    | Table 3-30  |
| Daily dermal, mg/day (DED)   | 1.9x10 <sup>-13</sup> | 1.1x10 <sup>-10</sup> | 4.7x10 <sup>-13</sup> | 5.9x10 <sup>-9</sup> | Calculated  |

TABLE 3-32. ESTIMATED TCDD EQUIVALENTS AND PERCENT EXPOSURE DUE TO 2378 TCDD FOR PAPER CONVERTING OPERATORS FROM DERMAL EXPOSURE

| Variable             | Daily exposure, <sup>a</sup><br>mg/day |                              | Lifetime<br>average daily<br>exposure, <sup>a</sup><br>mg/day-kg |                              |
|----------------------|--|------------------------------|--|------------------------------|
|                      | Low                                    | High                         | Low  | High                         |
| Toxicity equivalents | $2.3 \times 10^{-13}$<br>(29)          | $7.0 \times 10^{-10}$<br>(2) | $1.3 \times 10^{-15}$<br>(29)                                    | $4.7 \times 10^{-12}$<br>(2) |

<sup>a</sup> Values in parentheses are percent exposure to TCDD.

TABLE 3-33. ASSUMPTIONS AND UNCERTAINTIES IN ESTIMATING DERMAL EXPOSURE TO 2378 TCDD AND 2378 TCDF FOR PAPER CONVERTING WORKERS

| Uncertainty  | Associated assumption  | Reasonable possible variance of assumption   | Effects on results   |
|--|--|--|--|
| The skin surface area where the paper converting operator would be exposed to 2378 TCDD and 2378 TCDF. | The exposed skin surface area was estimated by PEI to be 100% of palm and finger surfaces of both hands. The high and low represent the difference between the surface area of a men's and women's hands. The exposed skin surface is 250 cm <sup>2</sup> for females and 300 cm <sup>2</sup> for males (NCASI 1988c). | The exposed skin surface area could potentially include exposure to both hands (front and back). The skin surface area would increase to 1,300 cm <sup>2</sup> (Popendorf 1982). | Exposure would range from 5 to 5.2 times the exposure level. |
| Dermal exposure duration for paper converting operators  | The duration of the exposure was assumed to be 8 hours since the operator spends the entire shift in the process area.   |  |  |



### 3.1.5 Nonwoven Industry

Workers in the nonwoven industry are potentially exposed to PCDDs and PCDFs through the handling of the pulp. Inhalation of dust may be possible during the machining of pulp; however, area dust samples for nonwoven operations are not available to identify any potential for dust inhalation.

Inhalation exposure to all workers in a nonwovens manufacturing facility may occur because of the mechanical processing of the dry pulp, which may create pulp dust in the workplace. Plants which produce personal and medical hygiene products such as diapers and surgical masks are required to follow Food and Drug Administration regulations on the amount of allowable area dust (Cunningham 1990). Typically, pulp dust resulting from the hammer mill is reclaimed through a vacuum screen formed by a vacuum filter. The filter has a 99+% efficiency and can filter particles as low as 1 to 1½ microns. These filters recycle the pulp dust to the hammer mill (Lammers 1989). Dermal exposure may occur to the operator feeding the pulp sheet manually into the hammer mill, but in automated nonwoven facilities the pulp is machine-fed into the hammer mill, and therefore there is no skin contact with the pulp. No information was available on the number of manual versus automated plants (Cunningham 1990).

#### 3.1.5.1 Level of Inhalation Exposure--

Inhalation exposure to PCDDs and PCDFs was based on the assumption that workers do not wear respiratory protection. The same calculation method as that used for paper converting operators was used to estimate the exposure levels for nonwoven workers. Exposure duration was assumed to be the entire

8-hour shift since no data were available. Table 3-34 summarizes the variables and results for inhalation exposure from pulp dust for the nonwoven workers. All workers in the nonwovens category were assumed to have similar exposures regardless of the type of product manufactured.

TABLE 3-34. ESTIMATED INHALATION EXPOSURE TO 2378 TCDD AND 2378 TCDF FOR NONWOVEN WORKERS FROM PULP DUST

| Variable   | 2378 TCDD             |                       | 2378 TCDF             |                       | Reference  |
|--|-----------------------|-----------------------|-----------------------|-----------------------|------------|
|  | Low                   | High                  | Low                   | High                  |            |
| Concentration of pulp dust, <sup>a</sup><br>mg/m <sup>3</sup> (Cm) | 0.2                   | 0.5                   | 0.2                   | 0.5                   | NIOSH 1985 |
| Amount of TCDD/TCDF in the mixture, (WF)                           | 1.0x10 <sup>-13</sup> | 4.9x10 <sup>-11</sup> | 2.5x10 <sup>-13</sup> | 2.62x10 <sup>-9</sup> | Table 2-5  |
| Exposure duration, h/day (ED)                                      | 8                     | 8                     | 8                     | 8                     | Table 3-36 |
| Daily inhalation, mg/day (Ip)                                      | 2.0x10 <sup>-13</sup> | 2.4x10 <sup>-10</sup> | 5.0x10 <sup>-13</sup> | 1.3x10 <sup>-8</sup>  | Calculated |

<sup>a</sup> These concentrations are below the OSHA nuisance dust standard of 15 mg/m<sup>3</sup>.

Equations 10 and 11 are used to calculate the TEQ and the percent exposure due to TCDD. Table 3-35 presents the TEQ and percent exposure due to 2,3,7,8 TCDD from particulate matter for the daily exposure and lifetime average daily exposure for the nonwoven workers. Table 3-36 presents the assumptions and uncertainties in the variables used to calculate the inhalation exposure from particulate matter for the nonwoven workers.

### 3.1.5.2 Level of Dermal Exposure--

Dermal exposure levels to PCDDs and PCDFs were based on the assumption that workers do not wear any types of gloves that effectively limit exposure to PCDDs and PCDFs. The same calculation method as that used for pulp mill operators' dermal exposure was used to estimate the exposure levels for the

TABLE 3-35. ESTIMATED TOXICITY EQUIVALENTS AND PERCENT EXPOSURE DUE TO 2378 TCDD FOR NONWOVEN WORKERS FROM PARTICULATE MATTER

| Variable             | Daily exposure, <sup>a</sup><br>mg/day |                             | Lifetime<br>average daily<br>exposure, <sup>a</sup><br>mg/day-kg |                              |
|----------------------|--|-----------------------------|--|------------------------------|
|                      | Low                                    | High                        | Low  | High                         |
| Toxicity equivalents | $2.5 \times 10^{-13}$<br>(29)          | $1.6 \times 10^{-9}$<br>(2) | $1.4 \times 10^{-15}$<br>(29)                                    | $1.0 \times 10^{-11}$<br>(2) |

<sup>a</sup> Values in parentheses are percent exposure to 2378 TCDD.

TABLE 3-36. ASSUMPTIONS AND UNCERTAINTIES IN ESTIMATING INHALATION EXPOSURE TO 2378 TCDD AND 2378 TCDF FOR NONWOVEN WORKERS FROM PARTICULATE MATTER

| Uncertainty   | Associated<br>assumption   | Reasonable<br>possible variance<br>of assumption | Effects on results |
|---|--|--|--------------------|
| Inhalation exposure duration for nonwoven operator. | The duration of the exposure was assumed to be 8 hours since the operator is in the process area the entire shift. |  |                    |

nonwoven workers. Since worker activity data were not available, it was assumed that the nonwoven worker would come into contact with the pulp 6 hours per day. Dermal exposure duration was based on engineering judgment, since no data were available. Table 3-37 summarizes the variables and results for dermal exposure for the nonwoven workers.

Equations 10 and 11 are used to calculate the TEQ and the percent exposure due to 2378 TCDD. Table 3-38 presents the daily and lifetime average daily TEQ and percent exposure due to 2378 TCDD from dermal exposure for nonwoven workers. Table 3-39 presents the assumptions and uncertainties in the variables used to calculate the dermal exposures for the nonwoven workers in Table 3-37.

#### 3.1.6 Commercial Users

During the commercial use of paper products, workers may be exposed to PCDDs and PCDFs through dermal contact with bleached paper products. The skin surface area contacting the bleached paper product and the amount of contact time varies with each job category. Almost all workers contact paper at some point in the work day. A wide variety of worker categories including secretaries, librarians, teachers, and accountants use various types of paper products for a large portion of the work day. Since many of the variables for the calculation of dermal exposure are not known, some assumptions were made. The number of workers in certain job categories was obtained from the United States Census Bureau and was the most complete and recent data. The concentration of 2378 TCDD and 2378 TCDF was estimated to be that of the pulp concentration because the PCDD and PCDF levels in paper products measured in the NCASI study was not representative of the entire paper industry. For medical workers, the concentration of 2378 TCDD and 2378 TCDF was assumed

TABLE 3-37. ESTIMATED DERMAL EXPOSURE TO 2378 TCDD AND 2378 TCDF FOR NONWOVEN WORKERS

| Variable  | 2378 TCDD             |                       | 2378 TCDF             |                       | Reference      |
|---|-----------------------|-----------------------|-----------------------|-----------------------|----------------|
|   | Low                   | High                  | Low                   | High                  |                |
| TCDD/TCDF concentration, ppt (DC)   | 0.012                 | 5.88                  | 0.03                  | 314                   | See Table 3-8  |
| Density of the pulp, mg/cm <sup>3</sup> ( $\rho$ )                                  | 1,000                 | 1,000                 | 1,000                 | 1,000                 | See Table 3-8  |
| Liquid film thickness of the pulp, cm (FT)  | 0.025                 | 0.025                 | 0.025                 | 0.025                 | See Table 3-8  |
| Liquid equilibrium partition coefficient of TCDD/TCDF from water, dimensionless (K) | 13,000                | 13,000                | 29,000                | 29,000                | EPA 1989c      |
| Absorption coefficient of TCDD/TCDF through the skin, h <sup>-1</sup> (AD)          | 0.012                 | 0.012                 | 0.012                 | 0.012                 | EPA 1989c      |
| Skin surface area, cm <sup>2</sup> (S)  | 250                   | 300                   | 250                   | 300                   | See Table 3-39 |
| Exposure duration, h/day (ED)   | 6                     | 6                     | 6                     | 6                     | See Table 3-39 |
| Dermal exposure, mg/day (DEW)   | $4.2 \times 10^{-16}$ | $2.4 \times 10^{-13}$ | $1.0 \times 10^{-15}$ | $1.3 \times 10^{-11}$ | Calculated     |

TABLE 3-38. ESTIMATED TOXICITY EQUIVALENTS AND PERCENT EXPOSURE DUE TO 2378 TCDD FOR NONWOVEN OPERATORS FROM DERMAL EXPOSURE

| Variable             | Daily exposure, <sup>a</sup><br>mg/day |                              | Lifetime average daily exposure, <sup>a</sup><br>mg/day-kg |                              |
|----------------------|--|------------------------------|--|------------------------------|
|                      | Low                                    | High                         | Low  | High                         |
| Toxicity equivalents | $5.2 \times 10^{-16}$<br>(29)          | $1.6 \times 10^{-12}$<br>(2) | $2.9 \times 10^{-18}$<br>(29)                              | $1.0 \times 10^{-14}$<br>(2) |

<sup>a</sup> Values in parentheses are percent exposure to 2378 TCDD.

TABLE 3-39. ASSUMPTIONS AND UNCERTAINTIES IN ESTIMATING DERMAL EXPOSURE TO 2378 TCDD AND 2378 TCDF FOR NONWOVEN WORKERS

| Uncertainty   | Associated assumption   | Reasonable possible variance of assumption   | Effects on results   |
|---|---|--|--|
| The skin surface area where the nonwoven workers would be exposed to 2378 TCDD and 2378 TCDF. | The exposed skin surface area was estimated by PEI to be 100% of palm and finger surfaces of both hands. The high and low represent the difference between the surface area of a men's and women's hands. The exposed skin surface is 250 cm <sup>2</sup> for females and 300 cm <sup>2</sup> for males (NCASI 1988). | The exposed skin surface area could potentially include exposure to both hands (front and back). The skin surface area would increase to 1,300 cm <sup>2</sup> (Popendorf 1982). | Exposure would range from 5 to 5.2 times the exposure level.       |
| Dermal exposure duration for nonwoven workers   | The duration of the exposure was assumed to be 6 hours since the operator spends a majority of the shift in the process area.   | Reasonable range in the duration would be 4 to 8 hours.  | Exposure would range between 0.7 and 1.4 times the exposure level. |

to be half since it was assumed that the nonwoven garments these workers contact are 50 percent pulp/50 percent textile fibers. The surface areas contacted by nonwoven garments and masks were assumed to be half of the face, and the entire palm and finger surfaces. Nonwoven garments worn by the medical workers were assumed to be used as a covering over clothing or other cloth garments. No data were available for exposure frequency and duration except for clerical workers and managers. All other exposure durations were based on engineering judgment and general knowledge of job related tasks involving the handling of paper and nonwoven products. The skin contact area for workers who are required to handle sheets of paper was assumed to be 20 percent of the total of palm and finger surfaces of both hands. These values were derived from studies done by NCASI on typical commercial users of paper products. The equation for handling dry material was used for commercial users of paper since they handle the dry paper. This equation is presented in Equation 16. Table 3-40 summarizes the variables and results for dermal exposure for commercial users of paper and nonwoven products.

Several of the job categories were combined because exposures were assumed to be similar. In Group 1, accountants, auditors, architects, librarians, archivists, and duplicating and mail/message distribution personnel were assumed to have similar exposures; Group 2 is made up of lawyers, judges, computer programmers and operators, record processors, management, and miscellaneous administrative support personnel. Secretaries, stenographers, and typists make up Group 3; Group 4 includes teachers and sales workers; and Group 5 includes medical workers.

Equations 10 and 11 are used to calculate TEQ and percent exposure due to 2378 TCDD. Table 3-41 presents daily lifetime average daily the TEQ and

TABLE 3-40. ESTIMATED DERMAL EXPOSURE TO 2378 TCDD AND 2378 TCDF  
FOR COMMERCIAL USERS OF PAPER AND NONWOVEN PRODUCTS

| Variable <sup>a</sup>   | 2378 TCDD             |                       | 2378 TCDF             |                       | Reference   |
|---|-----------------------|-----------------------|-----------------------|-----------------------|-------------|
|   | Low                   | High                  | Low                   | High                  |             |
| 2378 TCDD/2378 TCDF<br>concentration, ppt<br>(DC)                                   |                       |                       |                       |                       |             |
| -Group 1  | 0.1                   | 49                    | 0.25                  | 2,620                 | Table 2-5   |
| -Group 2  | 0.1                   | 49                    | 0.25                  | 2,620                 | Table 2-5   |
| -Group 3  | 0.1                   | 49                    | 0.25                  | 2,620                 | Table 2-5   |
| -Group 4  | 0.1                   | 49                    | 0.25                  | 2,620                 | Table 2-5   |
| -Group 5  | 0.05                  | 24.5                  | 0.25                  | 1,310                 | Table 3-42  |
| Weight of the dry<br>paper, g (PW)  | 4.5                   | 4.5                   | 4.5                   | 4.5                   | NCASI 1988c |
| Surface area of the<br>dry paper, cm <sup>2</sup> (PS)                              | 600                   | 600                   | 600                   | 600                   | NCASI 1988c |
| Rate of transfer<br>from the paper to<br>the skin, h <sup>-1</sup> (R)              | 0.0005                | 0.0005                | 0.0005                | 0.0005                | EPA 1989c   |
| Percent 2378 TCDD/2378<br>TCDF available for<br>dermal absorption,<br>percent (%AD) | 25                    | 25                    | 25                    | 25                    | EPA 1989c   |
| Skin surface area, cm <sup>2</sup> (S)  |                       |                       |                       |                       |             |
| -Group 1  | 63                    | 75                    | 63                    | 75                    | Table 3-42  |
| -Group 2  | 63                    | 75                    | 63                    | 75                    | Table 3-42  |
| -Group 3  | 38                    | 45                    | 38                    | 45                    | Table 3-42  |
| -Group 4  | 63                    | 75                    | 63                    | 75                    | Table 3-42  |
| -Group 5  | 338                   | 350                   | 338                   | 350                   | Table 3-42  |
| Exposure duration,<br>h/day (ED)  |                       |                       |                       |                       |             |
| -Group 1  | 6                     | 6                     | 6                     | 6                     | Table 3-42  |
| -Group 2  | 4                     | 4                     | 4                     | 4                     | Table 3-42  |
| -Group 3  | 3                     | 3                     | 3                     | 3                     | Table 3-42  |
| -Group 4  | 2                     | 2                     | 2                     | 2                     | Table 3-42  |
| -Group 5  | 8                     | 8                     | 8                     | 8                     | Table 3-42  |
| Dermal exposure, mg/day (DED)   |                       |                       |                       |                       |             |
| -Group 1  | $3.5 \times 10^{-14}$ | $2.1 \times 10^{-11}$ | $8.9 \times 10^{-14}$ | $1.1 \times 10^{-9}$  | Calculated  |
| -Group 2  | $2.4 \times 10^{-14}$ | $1.4 \times 10^{-11}$ | $5.9 \times 10^{-14}$ | $7.4 \times 10^{-10}$ | Calculated  |
| -Group 3  | $1.1 \times 10^{-14}$ | $6.2 \times 10^{-12}$ | $2.7 \times 10^{-14}$ | $3.3 \times 10^{-10}$ | Calculated  |
| -Group 4  | $1.2 \times 10^{-14}$ | $6.9 \times 10^{-12}$ | $3.0 \times 10^{-14}$ | $3.7 \times 10^{-10}$ | Calculated  |
| -Group 5  | $1.3 \times 10^{-13}$ | $6.4 \times 10^{-11}$ | $3.2 \times 10^{-13}$ | $3.4 \times 10^{-9}$  | Calculated  |

(continued)



- <sup>a</sup> Group 1 includes accountants, auditors, architects, librarians, archivists, curators, and duplicating and mail/message distribution occupations.  
Group 2 includes lawyers, judges, computer programmers, computer operators, record processing, management, and miscellaneous administrative support occupations.  
Group 3 includes secretaries, stenographers, and typists.  
Group 4 includes teachers and sales representatives and workers.  
Group 5 includes medical workers who may come in contact with nonwoven products.

TABLE 3-41. ESTIMATED TOXICITY EQUIVALENTS AND PERCENT EXPOSURE DUE TO 2378 TCDD FOR COMMERCIAL USERS OF PAPER FROM DERMAL EXPOSURE

| Variable <sup>a</sup> | Daily exposure, <sup>b</sup><br>mg/day |                              | Lifetime<br>average daily<br>exposure, <sup>b</sup><br>mg/day-Kg |                              |
|-----------------------|--|------------------------------|--|------------------------------|
|                       | Low                                    | High                         | Low  | High                         |
| Toxicity equivalents  |  |                              |  |                              |
| -Group 1              | $4.4 \times 10^{-14}$<br>(29)          | $1.3 \times 10^{-10}$<br>(2) | $2.5 \times 10^{-16}$<br>(29)                                    | $8.9 \times 10^{-13}$<br>(2) |
| -Group 2              | $3.0 \times 10^{-14}$<br>(29)          | $8.7 \times 10^{-11}$<br>(2) | $1.7 \times 10^{-16}$<br>(29)                                    | $5.9 \times 10^{-13}$<br>(2) |
| -Group 3              | $1.3 \times 10^{-14}$<br>(29)          | $3.9 \times 10^{-11}$<br>(2) | $7.5 \times 10^{-17}$<br>(29)                                    | $2.7 \times 10^{-13}$<br>(2) |
| -Group 4              | $1.5 \times 10^{-14}$<br>(29)          | $4.4 \times 10^{-11}$<br>(2) | $8.3 \times 10^{-17}$<br>(15)                                    | $3.0 \times 10^{-13}$<br>(2) |
| -Group 5              | $1.6 \times 10^{-13}$<br>(29)          | $4.1 \times 10^{-10}$<br>(2) | $8.9 \times 10^{-16}$<br>(29)                                    | $2.8 \times 10^{-12}$<br>(2) |

<sup>a</sup> Group 1 includes accountants, auditors, architects, librarians, archivists, curators, and duplicating and mail/message distribution occupations.

Group 2 includes lawyers, judges, computer programmers, computer operators, record processing, management and miscellaneous administrative support occupations.

Group 3 includes secretaries, stenographers, and typists.

Group 4 includes teachers and sales representatives and workers.

Group 5 includes medical workers who may come in contact with non-woven products.

<sup>b</sup> Values in parentheses are percent exposure to 2378 TCDD.

percent exposure due to 2378 TCDD from dermal exposure for commercial users of paper and nonwoven products. Table 3-42 presents the assumptions and uncertainties in the variables used to calculate the daily and lifetime average daily dermal exposure for commercial users of paper and nonwoven products in Table 3-40.

### 3.2 PERSONAL PROTECTIVE EQUIPMENT

Requirements for use of personal protective equipment vary from plant to plant. Use of protective equipment such as protective clothing or gloves for minimizing exposure to PCDDs and PCDFs through dermal contact was not mentioned in the literature; however, chemical-resistant gloves and other clothing are worn in pulp and paper manufacturing plants for protection from caustic and other corrosive chemicals (EPA 1989). Many plants provide respiratory devices for worker protection in emergency situations such as chlorine leaks (Soklow 1984). No information could be found regarding the extent of use of personal protective equipment such as dust masks or respirators in potential dust areas in the pulp and paper industry. At one papermaking plant studied by NIOSH, workers who performed the blowdown operations wore protective dust masks during this task. The other workers not performing this operation usually retreated to an unaffected area during the blowdown operation. The amount of dust inhaled by workers may be decreased through the use of better ventilation systems, wet methods or vacuums for cleaning dusts, and well-sealed dust masks (UPIU 1989).

### 3.3 METHOD OF ABSORPTION/INHALATION

The methods for dermal absorption of PCDDs/PCDFs fall into two categories: the transfer of PCDDs and PCDFs from the pulp through the sweat medium to the skin surface, and dry contact between the pulp or paper and the skin

TABLE 3-42. ASSUMPTIONS AND UNCERTAINTIES IN ESTIMATING DERMAL EXPOSURE TO 2378 TCDD AND 2378 TCDF FOR COMMERCIAL USERS OF PAPER PRODUCTS

| Uncertainty  | Associated assumption   | Reasonable possible variance of assumption  | Effects on results                     |
|--|---|---|--|
| 2378 TCDD/2378 TCDF concentration of Group 5 workers.  | The nonwoven material is made of 50 percent pulp and 50 percent other materials. Therefore, half of the 2378 TCDD/2378 TCDF concentration was used.   |   |  |
| The skin surface area where Group 1, Group 2, and Group 4 workers would be exposed to 2378 TCDD and 2378 TCDF. | The exposed skin surface area was estimated by PEI to be 25 percent of palm and finger surface area of both hands (NCASI 1988c). The high and low represent the difference between the surface area of men's and women's hands.   | The worst-case exposed skin surface area would include 100 percent exposure of palm and finger surfaces area of both hands. The skin surface area would increase to 250 cm <sup>2</sup> for males and 300 cm <sup>2</sup> for females (Popendorf 1982). | Maximum of 4 times greater exposure.   |
| The skin surface area where Group 3 workers would be exposed to 2378 TCDD and 2378 TCDF.                       | The exposed skin surface area was estimated by PEI to be 15 percent of palm and finger surface area of both hands (NCASI 1988c). The high and low represent the difference between the surface area of a men's and women's hands. | The worst-case exposed skin surface area would include 100 percent exposure of palm and finger surfaces area of both hands. The skin surface area would increase to 250 cm <sup>2</sup> for males and 300 cm <sup>2</sup> for females (Popendorf 1982). | Maximum of 6.6 times greater exposure. |

(continued)

TABLE 3-42 (continued)

| Uncertainty  | Associated assumption   | Reasonable possible variance of assumption   | Effects on results  |
|--|---|--|---|
| The skin surface area where Group 5 workers would be exposed to 2378 TCDD and 2378 TCDF. | The exposed skin surface area was estimated by PEI to be 25 percent of palm and finger surface area of both hands (NCASI 1988c) plus 25 percent exposure to the head. The high skin surface and low represent the difference between the surface area of a man and woman. | The worst-case exposed skin surface area would include 100 percent exposure of palm and finger surfaces area of both hands plus 25 percent exposure to the head. The surface area would increase to 250 cm <sup>2</sup> for males and 300 cm <sup>2</sup> for females (Popendorf 1982) | Maximum of 6.6 times greater exposure.                            |
| Dermal exposure duration for Group 1 workers.  | The duration of the exposure was assumed by PEI to be 6 hours since the majority of their job activities would require handling of paper.   | Reasonable range in the duration would be 4 to 8 hours.  | Exposure would range between 0.7 to 1.3 times the exposure level. |
| Dermal exposure duration for Group 2 workers.  | The duration of the exposure was assumed by PEI to be 4 hours since half of their job activities would require handling of paper.   | Reasonable range in the duration would be 2 to 8 hours.  | Exposure would range between 0.5 to 2 times the exposure level.   |
| Dermal exposure duration for Group 3 workers.  | The duration of the exposure was assumed by PEI to be 3 hours since less than half of their job activities would require handling of paper.   | Reasonable range in the duration would be 2 to 8 hours.  | Exposure would range between 0.7 to 2.7 times the exposure level. |

(continued)

TABLE 3-42 (continued)

| Uncertainty                                   | Associated assumption   | Reasonable possible variance of assumption               | Effects on results  |
|---|---|--|---|
| Dermal exposure duration for Group 4 workers. | The duration of the exposure was assumed by PEI to be 2 hours since less than half of their job activities would require handling of paper. | Reasonable range in the duration would be 1 to 4 hours.  | Exposure would range between 0.4 to 2 times the exposure level.   |
| Dermal exposure duration for Group 5 workers. | The duration of the exposure was assumed by PEI to be the entire 8 hour shift.  | Reasonable range in the duration would be 4 to 10 hours. | Exposure would range between 0.5 to 1.3 times the exposure level. |

surface. Several factors affect the skin's ability to absorb PCDDs and PCDFs, including skin barriers whose effectiveness are a function of age, damage, or disease; increased PCDD/PCDF concentration and surface area contact; or washing and rubbing of the skin. Absorption can also vary because of differences in skin thickness, and diffusivity for different areas of the body.

The amount of dust that workers inhale depends on several factors such as airborne concentration, the amount of time spent in the contaminated area, the particle size of dust and the proportion of breathing between nose and mouth and the volume of inhaled air. The method of inhalation, either through the mouth or the nose, can also affect the amount of dust inspired. Once a dust particle has been inhaled, four different modes of deposition can occur. Dust particles can deposit in the airways of the head and neck region, in the trachea, or in the lung; or they can be completely exhaled from the lungs without depositing within the body.

## SECTION 4

### CONCLUSIONS AND RECOMMENDATIONS

PCDDs and PCDFs are formed during the production of bleached pulp, thereby resulting in a potential for worker exposure to these chemicals in the production, processing, and commercial use of pulp, paper, and paper products. Studies have shown that the use of chlorine and chlorine-based bleaching agents could result in the generation of PCDDs and PCDFs such as 2378 TCDD, 2378 TCDF, and 1278 TCDF. This report focuses on 2378 TCDD and 2378 TCDF. Concentrations of PCDD and PCDF isomers have been detected in the bleached pulp and in the paper products themselves. Results from the 104 Mill Study showed that PCDD/PCDF concentrations in bleached pulp ranged from 0.10 to 49 ppt for 2378 TCDD and 0.25 to 2620 ppt for 2378 TCDF. The mean concentrations expressed as TEQ values for bleached pulp were 22.2 and 17.0 ppt for the Cooperative Dioxin Screening Study and 104 Mill Study, respectively. TEQ values represent the relative toxicity of 2378 TCDF with respect to 2378 TCDD, and were calculated by using Equation 1. The Cooperative Dioxin Screening Study had much fewer pulp samples than the 104 Mill Study (9 compared to 199), but the mean TEQ values were similar.

The kraft pulping process, which comprises 88 percent of all the bleached pulp processes, was the main focus of this report. Pulp and paper mill workers may be exposed to 2378 TCDD and 2378 TCDF primarily via three routes: 1) dermal contact with the bleaching wastewaters, bleached pulp or paper products; 2) inhalation of particulate containing 2378 TCDD/2378 TCDF



generated via paper dusts which are created during converting, rewinding, sizing, pulp-fluffing, cutting, or other operations; and 3) inhalation of 2378 TCDD/2378 TCDF volatilized from pulp and paper mills.

Although considerable data have been collected on PCDD and PCDF concentrations for pulp, sludge, and wastewaters in the pulp and paper industry, exposure data for PCDDs and PCDFs are nonexistent. This is in part because of a lack of a validated sampling and analytical method for measuring exposures. Because of the lack of available data to determine inhalation exposure from volatilization, PEI resorted to modeling techniques based on a number of assumptions in order to estimate inhalation and dermal exposures to 2378 TCDD and 2378 TCDF. A range (i.e., low and high values) of exposure and risk estimates are presented for each industry/worker scenario and exposure route.

One of the models used in this report for estimating exposures to vapors utilizes a mass balance approach to estimate worker exposure for specific activities (e.g., for pulp testers during sampling). A second approach is used for workers in a general area (e.g., bleach plant operators, utility operators) and is based on estimating a maximum 2378 TCDD/2378 TCDF partial pressure available for inhalation. In addition, the quantitative effects on volatilization of 2378 TCDD and 2378 TCDF due to binding with organic matter, and from interference due to other chemicals present in the pulp or paper were not available, and hence, not included in the calculations; thus, the inhalation exposure values provided are worst-case estimates. Some exposure estimates are based on the assumption that TCDDs, TCDFs, pulp, and water mixtures have two phases - an aqueous phase and a solid or pulp phase. Furthermore, TCDDs and TCDFs were assumed to reside only in the aqueous phase of the mixture.

Data were available on the amount of dust generated from the pulp and paper industry. These concentrations were below the OSHA nuisance dust standard of 15 mg/m<sup>3</sup>. No data were available on the amount of 2378 TCDD and 2378 TCDF in the pulp or paper dust; therefore, it was assumed that the concentration of 2378 TCDD and 2378 TCDF in the bleached pulp was equal to that in the paper and pulp dust. This approach results in an estimate of worst-case exposure levels for 2378 TCDD and 2378 TCDF.

There were no data available on dermal exposures for workers in the pulp and paper industry. PEI estimated exposures based on two CPSC models. These models consider the partitioning of PCDD/PCDF from the appropriate matrix (e.g., soil, sludges, paper) to a liquid (i.e., water, skin soil, urine, blood) and percutaneous absorption of PCDDs and PCDFs from the liquid. One model pertains to the handling of wet pulp or paper, while the other model pertains to the handling of dry pulp or paper. The extent of dermal exposure to workers varies depending on the handling of wet or dry material and the duration of the exposure. PEI assumed worst case exposure durations when no data on the duration was available.

Table 4-1 summarizes the 2378 TCDD and 2378 TCDF daily inhalation and dermal exposure levels estimated in Section 3 for workers involved in production, processing, and commercial use of pulp, paper, and paper products. Table 4-2 summarizes daily toxicity equivalents, lifetime average daily toxicity equivalents and the percentage of 2378 TCDD of these exposures estimated in this report for pulp and paper mill workers and commercial users of paper and nonwoven products. Appendix B presents the methodology for the calculation of average and population risks for workers involved in the production, processing, and commercial use of pulp, paper, and paper products. Table 4-3 summarizes the average risk and population risks based on

TABLE 4-1. SUMMARY OF 2378 TCDD AND 2378 TCDF DAILY INHALATION AND DERMAL EXPOSURE ESTIMATES FOR WORKERS INVOLVED IN MANUFACTURE, PROCESSING, AND COMMERCIAL USAGE OF PULP, PAPER, AND PAPER PRODUCTS

| Job category                                   | No. of workers | Exposure type                 | Daily exposure values (mg/day/worker) |                       |                       |                       | Duration of exposure (h/day) | Frequency of exposure (days/yr) |
|--|----------------|-------------------------------|---------------------------------------|-----------------------|-----------------------|-----------------------|------------------------------|---------------------------------|
|  |                |                               | 2378 TCDD                             |                       | 2378 TCDF             |                       |                              |                                 |
|  |                |                               | Low                                   | High                  | Low                   | High                  |                              |                                 |
| Pulp manufacturing<br>- Bleach plant operators | 434            | Inhalation-volatilization     | $2.0 \times 10^{-12}$                 | $2.0 \times 10^{-12}$ | $2.4 \times 10^{-9}$  | $2.4 \times 10^{-9}$  | 2                            | 250                             |
|  |                | Inhalation-particulate matter | N/A <sup>a</sup>                      | N/A                   | N/A                   | N/A                   | N/A                          | N/A                             |
|  | 433            | Derma1                        | $1.4 \times 10^{-16}$                 | $8.1 \times 10^{-14}$ | $1.6 \times 10^{-16}$ | $2.0 \times 10^{-12}$ | 2                            | 250                             |
|  |                | Inhalation-volatilization     | $2.0 \times 10^{-25}$                 | $1.9 \times 10^{-22}$ | $6.0 \times 10^{-22}$ | $1.3 \times 10^{-17}$ | 1                            | 250                             |
| - Pulp testers                                 | 433            | Inhalation-particulate matter | N/A                                   | N/A                   | N/A                   | N/A                   | N/A                          | N/A                             |
|  |                | Derma1                        | $1.1 \times 10^{-15}$                 | $5.3 \times 10^{-13}$ | $1.2 \times 10^{-15}$ | $1.3 \times 10^{-11}$ | 6                            | 250                             |
|  | 433            | Inhalation-volatilization     | $6.1 \times 10^{-12}$                 | $6.1 \times 10^{-12}$ | $7.2 \times 10^{-9}$  | $7.2 \times 10^{-9}$  | 6                            | 250                             |
|  |                | Inhalation-particulate matter | N/A                                   | N/A                   | N/A                   | N/A                   | N/A                          | N/A                             |
| Pulp drying<br>- Pulp drying operator          | 160            | Derma1                        | $2.2 \times 10^{-15}$                 | $1.1 \times 10^{-12}$ | $2.4 \times 10^{-15}$ | $2.5 \times 10^{-11}$ | 6                            | 250                             |
|  |                | Inhalation-volatilization     | $3.7 \times 10^{-17}$                 | $1.8 \times 10^{-14}$ | $1.1 \times 10^{-13}$ | $1.1 \times 10^{-9}$  | 2                            | 250                             |
|  | 80             | Inhalation-particulate matter | N/A                                   | N/A                   | N/A                   | N/A                   | N/A                          | N/A                             |
|  |                | Derma1                        | $4.7 \times 10^{-13}$                 | $2.8 \times 10^{-10}$ | $1.2 \times 10^{-12}$ | $1.5 \times 10^{-8}$  | 2                            | 250                             |
| - Pulp drying utility operator                 | 80             | Inhalation-volatilization     | $3.7 \times 10^{-17}$                 | $1.8 \times 10^{-14}$ | $1.1 \times 10^{-13}$ | $1.1 \times 10^{-9}$  | 2                            | 250                             |
|  |                | Inhalation-particulate matter | N/A                                   | N/A                   | N/A                   | N/A                   | N/A                          | N/A                             |
|  | 10,667         | Derma1                        | $1.4 \times 10^{-16}$                 | $8.1 \times 10^{-14}$ | $1.6 \times 10^{-16}$ | $2.0 \times 10^{-12}$ | 2                            | 250                             |
|  |                | Inhalation-volatilization     | $3.7 \times 10^{-17}$                 | $1.8 \times 10^{-14}$ | $1.1 \times 10^{-13}$ | $1.1 \times 10^{-9}$  | 2                            | 250                             |
| Paper manufacturer<br>- Wet end operator       | 10,667         | Inhalation-particulate matter | N/A                                   | N/A                   | N/A                   | N/A                   | N/A                          | N/A                             |
|  |                | Derma1                        | $1.4 \times 10^{-16}$                 | $8.1 \times 10^{-14}$ | $1.6 \times 10^{-16}$ | $2.0 \times 10^{-12}$ | 2                            | 250                             |
|  | 12,445         | Inhalation-volatilization     | $7.4 \times 10^{-17}$                 | $3.6 \times 10^{-14}$ | $2.2 \times 10^{-13}$ | $2.3 \times 10^{-9}$  | 4                            | 250                             |
|  |                | Inhalation-particulate matter | $1.0 \times 10^{-13}$                 | $1.2 \times 10^{-9}$  | $2.6 \times 10^{-13}$ | $6.4 \times 10^{-8}$  | 4                            | 250                             |
| - Dry end operator                             | 12,445         | Derma1                        | $9.4 \times 10^{-14}$                 | $5.5 \times 10^{-11}$ | $2.3 \times 10^{-13}$ | $2.9 \times 10^{-9}$  | 4                            | 250                             |

(continued)

TABLE 4-1 (continued)

| Job category                  | No. of workers | Exposure type                 | Daily exposure values (mg/day/worker) |                       |                       |                       |      | Duration of exposure (h/day) | Frequency of exposure (days/yr) |
|-------------------------------|----------------|-------------------------------|---------------------------------------|-----------------------|-----------------------|-----------------------|------|------------------------------|---------------------------------|
|                               |                |                               | 2378 TCDD                             |                       | 2378 TCDF             |                       |      |                              |                                 |
|                               |                |                               | Low                                   | High                  | Low                   | High                  | High |                              |                                 |
| -Utility operator             | 8,888          | Inhalation-volatilization     | 1.1x10 <sup>-16</sup>                 | 5.4x10 <sup>-14</sup> | 3.3x10 <sup>-13</sup> | 3.4x10 <sup>-9</sup>  | 6    | 250                          |                                 |
|                               |                | Inhalation-particulate matter | 3.9x10 <sup>-12</sup>                 | 6.7x10 <sup>-9</sup>  | 9.7x10 <sup>-12</sup> | 3.6x10 <sup>-7</sup>  | 1    | 250                          |                                 |
|                               |                | Dermal                        | 1.4x10 <sup>-13</sup>                 | 8.3x10 <sup>-11</sup> | 3.5x10 <sup>-13</sup> | 4.4x10 <sup>-9</sup>  | 6    | 250                          |                                 |
| Paper converting operations   |                |                               |                                       |                       |                       |                       |      |                              |                                 |
| - General worker              | 129,000        | Inhalation-volatilization     | N/A                                   | N/A                   | N/A                   | N/A                   | N/A  | N/A                          |                                 |
|                               |                | Inhalation-particulate matter | 2.0x10 <sup>-13</sup>                 | 3.9x10 <sup>-9</sup>  | 5.0x10 <sup>-13</sup> | 2.1x10 <sup>-7</sup>  | 8    | 250                          |                                 |
|                               |                | Dermal                        | 1.9x10 <sup>-13</sup>                 | 1.1x10 <sup>-10</sup> | 4.7x10 <sup>-13</sup> | 5.9x10 <sup>-9</sup>  | 8    | 250                          |                                 |
| Nonwoven operations           |                |                               |                                       |                       |                       |                       |      |                              |                                 |
| - General worker              | 15,000         | Inhalation-volatilization     | N/A                                   | N/A                   | N/A                   | N/A                   | N/A  | N/A                          |                                 |
|                               |                | Inhalation-particulate matter | 2.0x10 <sup>-13</sup>                 | 2.4x10 <sup>-10</sup> | 5.0x10 <sup>-13</sup> | 1.3x10 <sup>-8</sup>  | 8    | 250                          |                                 |
|                               |                | Dermal                        | 4.2x10 <sup>-16</sup>                 | 2.4x10 <sup>-13</sup> | 1.0x10 <sup>-15</sup> | 1.3x10 <sup>-11</sup> | 6    | 250                          |                                 |
| Commercial users <sup>b</sup> |                |                               |                                       |                       |                       |                       |      |                              |                                 |
| - Group 1                     | 2,639,000      | Dermal                        | 3.5x10 <sup>-14</sup>                 | 2.1x10 <sup>-11</sup> | 8.9x10 <sup>-14</sup> | 1.1x10 <sup>-9</sup>  | 6    | 250                          |                                 |
| - Group 2                     | 26,933,000     | Dermal                        | 2.4x10 <sup>-14</sup>                 | 1.4x10 <sup>-11</sup> | 5.9x10 <sup>-14</sup> | 7.4x10 <sup>-10</sup> | 4    | 250                          |                                 |
| - Group 3                     | 5,004,000      | Dermal                        | 1.1x10 <sup>-14</sup>                 | 6.2x10 <sup>-12</sup> | 2.7x10 <sup>-14</sup> | 3.3x10 <sup>-10</sup> | 3    | 250                          |                                 |
| - Group 4                     | 14,095,000     | Dermal                        | 1.2x10 <sup>-14</sup>                 | 6.9x10 <sup>-12</sup> | 3.0x10 <sup>-14</sup> | 3.7x10 <sup>-10</sup> | 2    | 250                          |                                 |
| - Group 5                     | 793,000        | Dermal                        | 1.3x10 <sup>-13</sup>                 | 6.4x10 <sup>-11</sup> | 3.2x10 <sup>-13</sup> | 3.4x10 <sup>-9</sup>  | 2    | 250                          |                                 |

<sup>a</sup> N/A = Not applicable.

<sup>b</sup> Group 1 includes accountants, auditors, architects, librarians, archivists, curators, and duplicating and mail/message distribution occupations.  
 Group 2 includes lawyers, judges, computer programmers, computer operators, records processing, management, miscellaneous administrative support occupations.  
 Group 3 includes secretaries, stenographers, and typists.  
 Group 4 includes teachers and sales representatives and workers.  
 Group 5 includes medical workers who may come in contact with nonwoven products.

TABLE 4-2. SUMMARY OF DAILY TOXICITY EQUIVALENTS LIFETIME AVERAGE DAILY TOXICITY EQUIVALENTS, AND PERCENTAGE EXPOSURE TO 2378 TCDD FOR WORKERS INVOLVED IN MANUFACTURE, PROCESSING, AND COMMERCIAL USAGE OF PULP, PAPER, AND PAPER PRODUCTS

| Job category                                   | Workers | Exposure type                           | Toxicity equivalents <sup>a</sup>                 |                                     |  |                              | Duration of exposure (h/day) | Frequency of exposure (days/yr) |
|--|---------|---|---|-------------------------------------|--|------------------------------|------------------------------|---------------------------------|
|  |         |   | Daily exposure, mg/day                            |                                     | Lifetime average daily exposure, mg/day kg |                              |                              |                                 |
|  |         |   | Low   | High                                | Low  | High                         |                              |                                 |
| Pulp manufacturing<br>- Bleach plant operators | 434     | Inhalation-volatilization               | 2.4x10 <sup>-10</sup><br>(0.08)                   | 2.4x10 <sup>-10</sup><br>(0.08)     | 1.4x10 <sup>-12</sup>                      | 1.6x10 <sup>-12</sup>        | 2                            | 250                             |
|  |         | Inhalation-particulate matter<br>Dermal | N/A <sup>b</sup><br>1.5x10 <sup>-16</sup><br>(47) | N/A<br>2.8x10 <sup>-13</sup><br>(4) | N/A<br>8.6x10 <sup>-19</sup>               | N/A<br>1.9x10 <sup>-15</sup> | N/A<br>2                     | N/A<br>250                      |
| - Pulp testers                                 | 433     | Inhalation-volatilization               | 6.1x10 <sup>-23</sup><br>(0.03)                   | 1.3x10 <sup>-18</sup><br>(0.002)    | 3.4x10 <sup>-25</sup>                      | 8.6x10 <sup>-21</sup>        | 1                            | 250                             |
|  |         | Inhalation-particulate matter<br>Dermal | N/A<br>1.2x10 <sup>-15</sup><br>(47)              | N/A<br>1.8x10 <sup>-12</sup><br>(4) | N/A<br>6.7x10 <sup>-18</sup>               | N/A<br>1.2x10 <sup>-14</sup> | N/A<br>6                     | N/A<br>250                      |
| - Utility operator                             | 433     | Inhalation-volatilization               | 7.3x10 <sup>-10</sup><br>(0.08)                   | 7.3x10 <sup>-10</sup><br>(0.08)     | 4.1x10 <sup>-12</sup>                      | 4.9x10 <sup>-12</sup>        | 6                            | 250                             |
|  |         | Inhalation-particulate matter<br>Dermal | N/A<br>2.4x10 <sup>-15</sup><br>(47)              | N/A<br>3.6x10 <sup>-12</sup><br>(4) | N/A<br>1.3x10 <sup>-17</sup>               | N/A<br>2.4x10 <sup>-14</sup> | N/A<br>6                     | N/A<br>250                      |
| Pulp drying<br>- Pulp drying operator          | 160     | Inhalation-volatilization               | 1.1x10 <sup>-14</sup><br>(0.03)                   | 1.1x10 <sup>-10</sup><br>(0.002)    | 6.1x10 <sup>-17</sup>                      | 7.7x10 <sup>-13</sup>        | 2                            | 250                             |
|  |         | Inhalation-particulate matter<br>Dermal | N/A<br>5.9x10 <sup>-13</sup><br>(29)              | N/A<br>1.8x10 <sup>-9</sup><br>(2)  | N/A<br>3.3x10 <sup>-15</sup>               | N/A<br>1.2x10 <sup>-11</sup> | N/A<br>2                     | N/A<br>250                      |
| - Pulp drying utility operator                 | 80      | Inhalation-volatilization               | 1.1x10 <sup>-14</sup><br>(0.03)                   | 1.1x10 <sup>-10</sup><br>(0.002)    | 6.1x10 <sup>-17</sup>                      | 7.7x10 <sup>-13</sup>        | 2                            | 250                             |
|  |         | Inhalation-particulate matter<br>Dermal | N/A<br>1.5x10 <sup>-16</sup><br>(47)              | N/A<br>2.8x10 <sup>-13</sup><br>(4) | N/A<br>8.6x10 <sup>-19</sup>               | N/A<br>1.9x10 <sup>-15</sup> | N/A<br>2                     | N/A<br>250                      |
| Paper manufacturer<br>- Wet end operator       | 10,667  | Inhalation-volatilization               | 1.1x10 <sup>-14</sup><br>(0.03)                   | 1.1x10 <sup>-10</sup><br>(0.002)    | 6.1x10 <sup>-17</sup>                      | 7.7x10 <sup>-13</sup>        | 2                            | 250                             |
|  |         | Inhalation-particulate matter<br>Dermal | N/A<br>1.5x10 <sup>-16</sup><br>(47)              | N/A<br>2.8x10 <sup>-13</sup><br>(4) | N/A<br>8.6x10 <sup>-19</sup>               | N/A<br>1.9x10 <sup>-15</sup> | N/A<br>2                     | N/A<br>250                      |

(continued)

TABLE 4-2 (continued)

| Job category                  | workers    | Exposure type                 | Toxicity equivalents <sup>a</sup> |                                  |  |                       | Duration of exposure (h/day) | Frequency of exposure (days/yr) |
|-------------------------------|------------|-------------------------------|-----------------------------------|----------------------------------|--|-----------------------|------------------------------|---------------------------------|
|                               |            |                               | Daily exposure, mg/day            |                                  | Lifetime average daily exposure, mg/day kg |                       |                              |                                 |
|                               |            |                               | Low                               | High                             | Low  | High                  |                              |                                 |
| - Dry end operator            | 12,445     | Inhalation-volatilization     | 2.2x10 <sup>-14</sup><br>(0.03)   | 2.3x10 <sup>-10</sup><br>(0.002) | 1.2x10 <sup>-16</sup>                      | 1.5x10 <sup>-12</sup> | 4                            | 250                             |
|                               |            | Inhalation-particulate matter | 1.3x10 <sup>-13</sup><br>(29)     | 7.6x10 <sup>-9</sup><br>(2)      | 7.3x10 <sup>-16</sup>                      | 5.1x10 <sup>-11</sup> | 4                            | 250                             |
|                               |            | Dermal                        | 1.2x10 <sup>-13</sup><br>(29)     | 3.5x10 <sup>-10</sup><br>(2)     | 6.6x10 <sup>-16</sup>                      | 2.4x10 <sup>-12</sup> | 4                            | 250                             |
| -Utility operator             | 8,888      | Inhalation-volatilization     | 3.3x10 <sup>-14</sup><br>(0.03)   | 3.4x10 <sup>-10</sup><br>(0.002) | 1.8x10 <sup>-16</sup>                      | 2.3x10 <sup>-12</sup> | 6                            | 250                             |
|                               |            | Inhalation-particulate matter | 4.8x10 <sup>-12</sup><br>(29)     | 4.2x10 <sup>-8</sup><br>(2)      | 2.7x10 <sup>-14</sup>                      | 2.9x10 <sup>-10</sup> | 1                            | 250                             |
|                               |            | Dermal                        | 1.8x10 <sup>-13</sup><br>(29)     | 5.2x10 <sup>-10</sup><br>(2)     | 9.8x10 <sup>-16</sup>                      | 3.5x10 <sup>-12</sup> | 6                            | 250                             |
| Paper converting operations   | 129,000    | Inhalation-volatilization     | N/A                               | N/A                              | N/A  | N/A                   | N/A                          | N/A                             |
| - General worker              |            | Inhalation-particulate matter | 2.5x10 <sup>-13</sup><br>(29)     | 2.5x10 <sup>-8</sup><br>(2)      | 1.4x10 <sup>-15</sup>                      | 1.7x10 <sup>-10</sup> | 8                            | 250                             |
|                               |            | Dermal                        | 2.3x10 <sup>-13</sup><br>(29)     | 7.0x10 <sup>-10</sup><br>(2)     | 1.3x10 <sup>-15</sup>                      | 4.7x10 <sup>-12</sup> | 8                            | 250                             |
| Nonwoven operations           | 15,000     | Inhalation-volatilization     | N/A                               | N/A                              | N/A  | N/A                   | N/A                          | N/A                             |
| - General worker              |            | Inhalation-particulate matter | 2.5x10 <sup>-13</sup><br>(29)     | 1.6x10 <sup>-9</sup><br>(2)      | 1.4x10 <sup>-15</sup>                      | 1.0x10 <sup>-11</sup> | 8                            | 250                             |
|                               |            | Dermal                        | 5.2x10 <sup>-16</sup><br>(29)     | 1.6x10 <sup>-12</sup><br>(2)     | 2.9x10 <sup>-18</sup>                      | 1.0x10 <sup>-14</sup> | 6                            | 250                             |
| Commercial users <sup>c</sup> | 2,639,000  | Dermal                        | 4.4x10 <sup>-14</sup><br>(29)     | 1.3x10 <sup>-10</sup><br>(2)     | 2.5x10 <sup>-16</sup>                      | 8.9x10 <sup>-13</sup> | 6                            | 250                             |
| - Group 1                     |            |                               |                                   |                                  |  |                       |                              |                                 |
| - Group 2                     | 26,933,000 | Dermal                        | 3.0x10 <sup>-14</sup><br>(29)     | 8.7x10 <sup>-11</sup><br>(2)     | 1.7x10 <sup>-16</sup>                      | 5.9x10 <sup>-13</sup> | 4                            | 250                             |
| - Group 3                     | 5,004,000  | Dermal                        | 1.3x10 <sup>-14</sup><br>(29)     | 3.9x10 <sup>-11</sup><br>(2)     | 7.5x10 <sup>-17</sup>                      | 2.7x10 <sup>-13</sup> | 3                            | 250                             |
| - Group 4                     | 14,095,000 | Dermal                        | 1.5x10 <sup>-14</sup><br>(29)     | 4.4x10 <sup>-11</sup><br>(2)     | 8.3x10 <sup>-17</sup>                      | 3.0x10 <sup>-13</sup> | 2                            | 250                             |
| - Group 5                     | 793,000    | Dermal                        | 1.6x10 <sup>-13</sup><br>(29)     | 4.1x10 <sup>-10</sup><br>(2)     | 8.9x10 <sup>-16</sup>                      | 2.8x10 <sup>-12</sup> | 2                            | 250                             |

(continued)

TABLE 4-2 (continued)

- <sup>a</sup> Values in parentheses are percent exposure to 2378 TCDD.
- <sup>b</sup> N/A = Not applicable.
- <sup>c</sup> Group 1 includes accountants, auditors, architects, librarians, archivists, curators, and duplicating and mail/message distribution occupations.  
 Group 2 includes lawyers, judges, computer programmers, computer operators, records processing, management, miscellaneous administrative support occupations.  
 Group 3 includes secretaries, stenographers, and typists.  
 Group 4 includes teachers and sales representatives and workers.  
 Group 5 includes medical workers who may come in contact with nonwoven products such as garments and masks.

TABLE 4-3. SUMMARY OF OUTER BOUNDS OF AVERAGE INDIVIDUAL AND POPULATION RISKS BASED ON TOXICITY EQUIVALENTS FOR WORKERS INVOLVED IN MANUFACTURING, PROCESSING, AND COMMERCIAL USAGE OF PULP, PAPER, AND PAPER PRODUCTS<sup>a</sup>

| Job category             | No. of workers | Exposure type                 | Average risk                  |                                | Population risk <sup>b</sup> |                     |
|--------------------------|----------------|-------------------------------|-------------------------------|--------------------------------|------------------------------|---------------------|
|                          |                |                               | Low                           | High                           | Low                          | High                |
| Pulp manufacturing       |                |                               |                               |                                |                              |                     |
| - Bleach plant operators | 434            | Inhalation-volatilization     | 4x10 <sup>-7</sup><br>(0.08)  | 5x10 <sup>-7</sup><br>(0.08)   | 4x10 <sup>-6</sup>           | 5x10 <sup>-6</sup>  |
|                          |                | Inhalation-particulate matter | N/A <sup>c</sup>              | N/A                            | N/A                          | N/A                 |
|                          |                | Dermal                        | 2x10 <sup>-13</sup><br>(47)   | 5x10 <sup>-10</sup><br>(4)     | 3x10 <sup>-12</sup>          | 6x10 <sup>-9</sup>  |
| - Pulp testers           | 433            | Inhalation-volatilization     | 1x10 <sup>-19</sup><br>(0.03) | 2x10 <sup>-15</sup><br>(0.002) | 1x10 <sup>-18</sup>          | 3x10 <sup>-14</sup> |
|                          |                | Inhalation-particulate matter | N/A                           | N/A                            | N/A                          | N/A                 |
|                          |                | Dermal                        | 2x10 <sup>-12</sup><br>(47)   | 3x10 <sup>-9</sup><br>(4)      | 2x10 <sup>-11</sup>          | 4x10 <sup>-8</sup>  |
| - Utility operator       | 433            | Inhalation-volatilization     | 1x10 <sup>-6</sup><br>(0.08)  | 1x10 <sup>-6</sup><br>(0.08)   | 1x10 <sup>-5</sup>           | 2x10 <sup>-5</sup>  |
|                          |                | Inhalation-particulate matter | N/A                           | N/A                            | N/A                          | N/A                 |
|                          |                | Dermal                        | 4x10 <sup>-12</sup><br>(47)   | 7x10 <sup>-9</sup><br>(4)      | 4x10 <sup>-11</sup>          | 7x10 <sup>-8</sup>  |
| Pulp drying              |                |                               |                               |                                |                              |                     |
| - Pulp drying operator   | 160            | Inhalation-volatilization     | 2x10 <sup>-11</sup><br>(0.03) | 2x10 <sup>-7</sup><br>(0.002)  | 7x10 <sup>-11</sup>          | 9x10 <sup>-7</sup>  |
|                          |                | Inhalation-particulate matter | N/A                           | N/A                            | N/A                          | N/A                 |
|                          |                | Dermal                        | 9x10 <sup>-10</sup><br>(29)   | 3x10 <sup>-6</sup><br>(2)      | 4x10 <sup>-9</sup>           | 1x10 <sup>-5</sup>  |

(continued)



TABLE 4-3 (continued)

| Job category                   | No. of workers | Exposure type                 | Average risk                  |                               | Population risk <sup>b</sup> |                    |
|--------------------------------|----------------|-------------------------------|-------------------------------|-------------------------------|------------------------------|--------------------|
|                                |                |                               | Low                           | High                          | Low                          | High               |
| - Pulp drying utility operator | 80             | Inhalation-volatilization     | $2 \times 10^{-11}$<br>(0.03) | $2 \times 10^{-7}$<br>(0.002) | $3 \times 10^{-11}$          | $4 \times 10^{-7}$ |
|                                |                | Inhalation-particulate matter | N/A                           | N/A                           | N/A                          | N/A                |
|                                |                | Dermal                        | $2 \times 10^{-13}$<br>(29)   | $5 \times 10^{-10}$<br>(2)    | $5 \times 10^{-13}$          | $1 \times 10^{-9}$ |
| Paper manufacturer             |                |                               |                               |                               |                              |                    |
| - Wet-end operator             | 10,667         | Inhalation-volatilization     | $2 \times 10^{-11}$<br>(0.03) | $2 \times 10^{-7}$<br>(0.002) | $5 \times 10^{-9}$           | $6 \times 10^{-5}$ |
|                                |                | Inhalation-particulate matter | N/A                           | N/A                           | N/A                          | N/A                |
|                                |                | Dermal                        | $2 \times 10^{-13}$<br>(47)   | $5 \times 10^{-10}$<br>(4)    | $7 \times 10^{-11}$          | $1 \times 10^{-7}$ |
| - Dry-end operator             | 12,445         | Inhalation-volatilization     | $3 \times 10^{-11}$<br>(0.03) | $4 \times 10^{-7}$<br>(0.002) | $1 \times 10^{-8}$           | $1 \times 10^{-4}$ |
|                                |                | Inhalation-particulate matter | $2 \times 10^{-10}$<br>(29)   | $1 \times 10^{-5}$<br>(2)     | $6 \times 10^{-8}$           | $5 \times 10^{-3}$ |
|                                |                | Dermal                        | $2 \times 10^{-10}$<br>(29)   | $7 \times 10^{-7}$<br>(2)     | $6 \times 10^{-8}$           | $2 \times 10^{-4}$ |
| - Utility operator             | 8,888          | Inhalation-volatilization     | $5 \times 10^{-11}$<br>(0.03) | $7 \times 10^{-7}$<br>(0.002) | $1 \times 10^{-8}$           | $1 \times 10^{-4}$ |
|                                |                | Inhalation-particulate matter | $8 \times 10^{-9}$<br>(29)    | $8 \times 10^{-5}$<br>(2)     | $2 \times 10^{-6}$           | $2 \times 10^{-2}$ |
|                                |                | Dermal                        | $3 \times 10^{-10}$<br>(29)   | $1 \times 10^{-6}$<br>(2)     | $6 \times 10^{-8}$           | $2 \times 10^{-4}$ |
| Paper converting operations    |                |                               |                               |                               |                              |                    |
| - General worker               | 129,000        | Inhalation-volatilization     | N/A                           | N/A                           | N/A                          | N/A                |
|                                |                | Inhalation-particulate matter | $4 \times 10^{-10}$<br>(29)   | $5 \times 10^{-5}$<br>(2)     | $1 \times 10^{-6}$           | $2 \times 10^{-1}$ |
|                                |                | Dermal                        | $4 \times 10^{-10}$<br>(29)   | $1 \times 10^{-6}$<br>(2)     | $1 \times 10^{-6}$           | $4 \times 10^{-3}$ |

(continued)

TABLE 4-3 (continued)

| Job category                  | No. of workers | Exposure type                 | Average risk                |                           | Population risk <sup>b</sup> |                    |
|-------------------------------|----------------|-------------------------------|-----------------------------|---------------------------|------------------------------|--------------------|
|                               |                |                               | Low                         | High                      | Low                          | High               |
| Nonwoven operations           |                |                               |                             |                           |                              |                    |
| - General worker              | 15,000         | Inhalation-volatilization     | N/A                         | N/A                       | N/A                          | N/A                |
|                               |                | Inhalation-particulate matter | $4 \times 10^{-10}$<br>(29) | $3 \times 10^{-6}$<br>(2) | $1 \times 10^{-7}$           | $1 \times 10^{-3}$ |
|                               |                | Dermal                        | $8 \times 10^{-13}$<br>(29) | $3 \times 10^{-9}$<br>(2) | $3 \times 10^{-10}$          | $1 \times 10^{-6}$ |
| Commercial users <sup>d</sup> |                |                               |                             |                           |                              |                    |
| - Group 1                     | 2,639,000      | Dermal                        | $7 \times 10^{-11}$<br>(29) | $3 \times 10^{-7}$<br>(2) | $5 \times 10^{-6}$           | $2 \times 10^{-2}$ |
| - Group 2                     | 26,933,000     | Dermal                        | $5 \times 10^{-11}$<br>(29) | $2 \times 10^{-7}$<br>(2) | $3 \times 10^{-6}$           | $1 \times 10^{-2}$ |
| - Group 3                     | 5,004,000      | Dermal                        | $2 \times 10^{-11}$<br>(29) | $8 \times 10^{-8}$<br>(2) | $1 \times 10^{-6}$           | $5 \times 10^{-3}$ |
| - Group 4                     | 14,095,000     | Dermal                        | $2 \times 10^{-11}$<br>(29) | $8 \times 10^{-8}$<br>(2) | $2 \times 10^{-6}$           | $6 \times 10^{-3}$ |
| - Group 5                     | 793,000        | Dermal                        | $3 \times 10^{-10}$<br>(29) | $8 \times 10^{-7}$<br>(2) | $2 \times 10^{-5}$           | $5 \times 10^{-2}$ |

<sup>a</sup> Values in parentheses are percent exposure to 2378 TCDD.

<sup>b</sup> Values represent cases per year.

<sup>c</sup> N/A = not applicable

<sup>d</sup> Group 1 includes accountants, auditors, architects, librarians, archivists, curators, and duplicating and mail/message distribution occupations.  
Group 2 includes lawyers, judges, computer programmers, computer operators, records processing, management, miscellaneous administrative support occupations.  
Group 3 includes secretaries, stenographers, and typists.  
Group 4 includes teachers and sales representatives.  
Group 5 includes medical workers who may come in contact with nonwoven products such as garments and masks.

lifetime average daily toxicity equivalents for pulp and paper mill workers and commercial users of paper and nonwoven products.

There are several data needs for developing more refined estimates of worker exposure to PCDDs and PCDFs in the pulp and paper industry. Some areas in which additional information is needed include the following: 1) characterization of worker activities in pulp (nonwovens) converting operations; 2) the frequency and duration of potential dermal and inhalation worker exposure to PCDDs and PCDFs in the pulp and paper manufacturing, converting, and nonwoven fabric and textile fiber industries; 3) the extent of use and effectiveness of personal protective equipment and engineering controls in this industry; and 4) the number of workers in each job category potentially exposed to PCDDs and PCDFs. Additional information is also needed on the potential for exposure to pulp and paper workers during infrequent activities such as bi-yearly cleaning of grinding pit and paper roll residuals which may contain high PCDD/PCDF concentrations (Sullivan 1989).

There are some ongoing as well as planned studies which may clarify some of the uncertainties found in this report. A NIOSH study to characterize worker exposure to PCDDs and PCDFs at up to 4 kraft pulp/paper mills is currently underway and is expected to be completed in 1990. The 104-Mill Study has been completed; however, the data that was collected needs to be analyzed with respect to plant operating parameters such as production rate, type of wood used (e.g., softwood, hardwood), and quantity of bleaching chemical used to determine variations in 2378 TCDD/2378 TCDF concentrations (and hence risks) as a function of plant operations. A follow-up study to the 104-Mill Study is being performed in early 1990 by members of NCASI, the American Paper Institute (API), and participating pulp mills. This study will provide new PCDD/PCDF concentration data at selected pulp and paper

mills which will reflect advancements in PCDD/PCDF reduction. Elimination of petroleum-based additives such as oil-based defoamers and pitch dispersant has been achieved at some pulp mills. Also, reduction in chlorine usage during the bleaching stage has been pursued at some mills with favorable PCDD/PCDF reduction. This new study should provide some insight on the amount and extent of PCDD/PCDF reduction in the pulp and paper industry. Also, this new information should provide updated PCDD/PCDF concentrations for the exposure calculations (Grant 1990). The 25 Bleach Line Study conducted by NCASI will be completed in early 1990 and will provide PCDD/PCDF concentration data for 25 bleach lines in 31 mills. PEI is also awaiting additional information on workforce characterization, converting operations, and production data from the API which should assist in filling some of the data gaps. Site visits to pulp manufacturing, papermaking, and paper converting operations would also provide additional insight on the potential for exposure to workers when performing different activities.

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## APPENDIX A

104 MILL STUDY: 2378 TCDD AND 2378 TCDF  
CONCENTRATION IN BLEACHED PULP ON A DRY BASIS

104 MILL STUDY: 2378 TCDD AND 2378 TCDF  
CONCENTRATIONS IN BLEACHED PULP ON A DRY BASIS

| Company and location                              | Ranges in pulp (ppt)  |                       |
|---|-----------------------|-----------------------|
|   | 2378 TCDD             | 2378 TCDF             |
| Alabama River Pulp<br>Claiborne, AL               | 38-43.0               | 97-120.0              |
| Alaska Pulp Corp.<br>Sitka, AK                    | 0.7                   | 1.4                   |
| Appleton Papers, Inc.<br>Roaring Springs, PA      | 1.0                   | 21.0                  |
| Badger Paper Mills, Inc.<br>Peshtigo, WI          | 4.5                   | 110.0-323.0           |
| Boise Cascade Corp.<br>Jackson, AL                | 9.1-11.0              | 71.0-104.0            |
| DeRidder, LA                                      | 5.3                   | 8.7                   |
| St. Helens, OR                                    | 4.2-6.5               | 11.0-18.0             |
| Rumford, ME                                       | 17.0-116.0            | 111.0-800.0           |
| Wallula, WA                                       | 56.0                  | 1380.0                |
| International Falls, MN                           | NA <sup>a</sup>       |                       |
| Bowater Corp.<br>Catawba, SC                      | 2.1                   | 3.3                   |
| Calhoun, TN                                       | 7.7                   | 53.0                  |
| Brunswick Pulp/Paper<br>Brunswick, GA             | 1.6-8.3               | 2.9-12.0              |
| Buckeye Cellulose (P&G)<br>Perry, FL              | 0.5 <sup>b</sup>      | 2.5 <sup>b</sup>      |
| Oglethorpe, GA                                    | 0.5 <sup>b</sup>      | 0.9 <sup>b</sup>      |
| Champion Intl. Corp.<br>Lufkin, TX                | 4.9                   | 6.8                   |
| Courtland, AL                                     | 3.5-23.0              | 7.6-102.0             |
| Quinnesec, MI                                     | 7.8                   | 45.0-50.0             |
| Cantonment, FL                                    | 0.7 <sup>b</sup> -4.9 | 0.7 <sup>b</sup> -4.1 |
| Houston, TX                                       | 4.9                   | 6.8                   |
| Canton, NC  | 4.6-17.0              | 5.5-27.0              |
| Chesapeake Corp.<br>West Point, VA                | 8.3                   | 14.0                  |
| Consolidated Papers, Inc.<br>Wisconsin Rapids, WI | 18.0-20.0             | 79.0-83.0             |
| Container Corp. of America<br>Brewton, AL         | 2.3                   | 4.5                   |
| Flambeau Paper Corp.<br>Park Falls, WI            | 0.5 <sup>b</sup>      | 0.9 <sup>b</sup>      |
| Federal Paper Board Co.<br>Augusta, GA            | 2.4-7.9               | 7.9-19.0              |
| Riegelwood, NC                                    | 3.2-4.3               | 1.3-4.7               |
| Finch, Pruyn & Co., Inc.<br>Glens Falls, NY       | 0.3 <sup>b</sup>      | 0.3 <sup>b</sup>      |
| Gaylord Container<br>Antioch, CA                  | 32.0                  | 969.0                 |
| Georgia-Pacific Corp.<br>Bellingham, WA           | 6.2 <sup>b</sup>      | 449.0                 |
| Crossett, AR                                      | 6.0-19.0              | 59.0-308.0            |
| Palatka, FL                                       | 0.5 <sup>b</sup>      | 0.9 <sup>b</sup> -2.4 |
| Woodland, ME                                      | 0.4 <sup>b</sup>      | 0.9                   |
| Zachary, LA (Port Hudson)                         | 5.2-27.0              | 78.0-632.0            |
| Gilman Paper Co.<br>St. Marys, GA                 | 2.8-3.7               | 6.8-12.0              |
| Gulf States Paper Corp.<br>Demopolis, AL          | 5.2                   | 20.0                  |
| Hammermill Papers (IP)<br>Erie, PA                | 6.4                   | 22.0                  |
| Selma, AL   | 2.1-4.7               | 21.0-22.0             |

(continued)

| Company and location                                   | Ranges in pulp (ppt)   |                  |
|--|------------------------|------------------|
|  | 2378 TCDD              | 2378 TCDF        |
| International Paper Co.                                |                        |                  |
| Bastrop, LA  | 5.1-6.3                | 22.0-42.0        |
| Georgetown, SC   | 1.9-17.0               | 7.7-55.0         |
| Jay, ME  | NA <sup>a</sup>        |                  |
| Mobile, AL   | 3.5-21.0               | 14.0-106.0       |
| Moss Point, MS   | 7.3-15.0               | 36.0-105.0       |
| Natchez, MS  | 3.6                    | 15.0             |
| Pine Bluff, AR   | 5.0-23.0               | 5.7-0-661.0      |
| Texarkana, TX  | 7.0-12.0               | 51.0-81.0        |
| Ticonderoga, NY  | 16.0-31.0              | 103.0-185.0      |
| ITT-Rayonier, Inc.                                     |                        |                  |
| Fernandina Beach, FL                                   | 0.2 <sup>b</sup>       | 0.5 <sup>b</sup> |
| Hoquiam, WA  | 0.3 <sup>b</sup>       | 3.8              |
| Jesup, GA  | 0.3 <sup>b</sup>       | 0.6-0.9          |
| Port Angeles, WA                                       | 0.6 <sup>b</sup>       | 2.1              |
| James River Corp.                                      |                        |                  |
| Berlin, NH   | 3.3-32.0               | 41.0-1110.0      |
| Camas, WA  | 0.0 <sup>b</sup> -12.0 | 0.6-152.0        |
| Clatskanie, OR   | NA <sup>a</sup>        |                  |
| Green Bay, WI  | 0.8 <sup>b</sup>       | 7.1              |
| Old Town, ME   | 13.0                   | 51.0             |
| St. Francisville, LA                                   | 4.9-6.4                | 15.0-19.0        |
| Butler, AL   | 1.2-3.7                | 1.4-30.0         |
| Kimberly-Clark Corp.                                   |                        |                  |
| Coosa Pines, AL  | 0.3 <sup>b</sup> -11.0 | 1.0-38.0         |
| Leaf River Forest Products<br>(Great Northern Nekoosa) |                        |                  |
| New Augusta, MS  | 3.6                    | 15.0             |
| Lincoln Pulp/Paper                                     |                        |                  |
| Lincoln, ME  | 16.0                   | 94.0             |
| Longview Fibre Co.                                     |                        |                  |
| Longview, WA   | 4.8                    | 18.0             |
| Louisiana-Pacific Corp.                                |                        |                  |
| Ketchikan, AK  | 0.3 <sup>b</sup>       | 0.3 <sup>b</sup> |
| Samoa, CA  | 9.1                    | 59.0             |
| Mead Corp.   |                        |                  |
| Chillicothe, OH  | NA <sup>a</sup>        |                  |
| Escanaba, MI   | 15.0-25.0              | 39.0-116.0       |
| Kingsport, TN  | 1.5                    | 25.0             |
| Nekoosa Papers, Inc.<br>(Great Northern Nekoosa)       |                        |                  |
| Ashdown, AR  | 2.8-5.5                | 12.0-27.0        |
| Nekoosa, WI  | 22.0                   | 283.0            |
| Port Edwards, WI                                       | 0.4 <sup>b</sup>       | 4.1              |
| Penntech Papers, Inc.                                  |                        |                  |
| Johnsonburg, PA  | 3.1                    | 38.0             |
| Pope & Talbot, Inc.                                    |                        |                  |
| Halsey, OR   | 10.0                   | 41.0             |
| Potlatch Corp.   |                        |                  |
| Cloquet, MN  | 1.2-2.4                | 5.0-7.9          |
| Lewiston, ID   | 25.0-27.0              | 147.0-153.0      |
| McGhee, AR   | 12.0-21.0              | 59.0-83.0        |
| P.H. Glatfelter Co.                                    |                        |                  |
| Spring Grove, PA                                       | 0.4-6.5                | 2.2-18.0         |
| Procter & Gamble Co.                                   |                        |                  |
| Mehoopany, PA  | 2.0                    | 1.1              |
| Scott Paper Co.  |                        |                  |
| Everett, WA  | 0.3 <sup>b</sup>       | 0.1 <sup>b</sup> |
| Mobile, AL   | 0.6-1.7                | 0.8-2.2          |

(continued)

| Company and location      | Ranges in pulp (ppt)               |            |
|---------------------------|------------------------------------|------------|
|                           | 2378 TCDD                          | 2378 TCDF  |
| S.D. Warren (Scott Paper) |                                    |            |
| Hinckley, ME              | 1.9-8.5                            | 10.0-37.0  |
| Muskegon, MI              | 0.3 <sup>b</sup>                   | 1.0        |
| Westbroo, ME              | 4.2-8.1                            | 16.0-30.0  |
| Simpson Paper Co.         |                                    |            |
| Anderson, CA              | 49.0                               | 2620.0     |
| Fairhaven, CA             | 20.0                               | 106.0      |
| Pasadena, TX              | 4.5-18.0                           | 11.0-66.0  |
| Tacoma, WA                | 12.0                               | 38.0       |
| St. Joe Paper Co.         |                                    |            |
| Port St. Joe, FL          | 2.2                                | 5.7        |
| Stone Container Corp.     |                                    |            |
| Missoula, MT              | 4.1                                | 13.0       |
| Panama City, FL           | 0.1 <sup>b</sup>                   | 6.6        |
| Snowflake, AZ             | 0.7 <sup>b</sup>                   | 1.3        |
| Temple-Eastex, Inc.       |                                    |            |
| Evadale, TX               | 1.9-7.8                            | 6.3-22.0   |
| Union Camp Corp.          |                                    |            |
| Eastover, SC              | 0.4 <sup>b</sup> -2.4              | 1.3-5.6    |
| Franklin, VA              | 1.1-5.4                            | 2.1-69     |
| Wausau Paper Mills Co.    |                                    |            |
| Brokaw, WI                | 0.1 <sup>b</sup>                   | 9.9        |
| Westvaco Corp.            |                                    |            |
| Covington, VA             | 5.9-13.0                           | 19.0-105.0 |
| Luke, MD                  | 29.0                               | 157.0      |
| Wickliffe, KY             | 2.1-12.0                           | 25.0-55.0  |
| Weyerhaeuser Co.          |                                    |            |
| Cosmopolis, WA            | 0.3 <sup>b</sup> -1.0 <sup>b</sup> | 2.9-6.4    |
| Everett, WA               | 3.4-5.2                            | 16.0-20.0  |
| Longview, WA              | 1.6-7.7                            | 2.8-20.0   |
| New Bern, NC              | 7.5                                | 45.0       |
| Plymouth, NC              | 10.0-33.0                          | 82.0-318.0 |
| Rothchild, WI             | 15.0                               | 26.0       |
| Willamette, Ind.          |                                    |            |
| Hawesville, KY            | 0.3 <sup>b</sup> -0.5 <sup>b</sup> | 1.1-1.9    |

<sup>a</sup> NA - Not available.

<sup>b</sup> Indicates nondetectable.

Note: For pulp analysis, the EPA results do not accurately distinguish between levels of dioxin and furan found in hardwood and softwood pulps, so the lowest and highest levels reported are presented to represent the ranges found at each mill.

APPENDIX B  
RISK ASSESSMENT METHODOLOGY

## APPENDIX B

### RISK ASSESSMENT

This section presents the methodology for the calculation of risk to 2378 TCDD and 2378 TCDF. Unit risk is used to compare the relative potencies of carcinogens. Potency is defined as the linear portion of a given dose-response curve which is used to calculate the unit risk factors. On a curve, the upper confidence limit for the extra risk calculated at low doses is always linear. The slope ( $q^*$ ) is taken as the upper-bound of the potency of the chemical (TCDD) in inducing cancer at low doses. The 95% upper confidence limit of dose-response functions for the linear slope factor  $q^*$  of 2378 TCDD is 0.156 kg- d/ng or  $1.56 \times 10^{+5} \text{ (mg/kg/day)}^{-1}$ . The derivation of this factor is described in EPA 1984.

During the development of the slope factor an absorption factor of 55 percent was applied. The percent of the TEQ available for absorption was incorporated into the equations in Chapter 3 for inhalation and dermal exposures. The equation for calculation of average risk and population risk are presented in Equations B-1 and B-2, respectively.

$$\text{AVGRISK} = \text{LTEQ} \times \text{PF} / \text{AF} \quad \text{Equation B-1}$$

$$\text{POPRISK} = \text{AVGRISK} \times \text{POP} / \text{YEAR} \quad \text{Equation B-2}$$

Where:

AVGRISK = average risk for lifetime average daily toxicity equivalents,  
unitless

LTEQ = lifetime average daily TEQ, mg/day-kg

PF = potency factor, kg-day/mg

AF = absorption factor, unitless

POPRISK = population risk for lifetime average daily toxicity  
equivalents, cases/year

POP = number of workers in the population

YEAR = number of years for worker exposure, years

B-2

The lifetime average daily toxicity equivalents (LTEQ) which were used in Equation B-1 were presented in tables from Section 3. Three types of lifetime average daily TEQs were calculated in Section 3 for inhalation exposure from volatilization, inhalation exposure from particulate matter, and dermal exposure. The potency factor used in the equation was 0.156 kg-day/ng (EPA 1984). The absorption factor (AF) was estimated to be 0.55 (Farland 1987).

Table B-1 summarizes the variables for the estimated average risk and population risk for workers involved in production, processing, and commercial use of pulp, paper, and paper products. The average risks and population risks are summarized in Table 5-3. The following is an example calculation for calculating average risk and population risks.

Lower limit for average risk for bleach plant operators from volatilization

$$\begin{aligned} \text{AVGRISK} &= 1.4 \times 10^{-12} \text{ mg/day-kg} \times 1.56 \times 10^5 \text{ kg-day/mg/0.55} \\ &= 4 \times 10^{-7} \end{aligned}$$

Lower limit for population risk for bleach plant operators from volatilization

$$\begin{aligned} \text{POPRISK} &= 4 \times 10^{-7} \times 434 \text{ workers/40 years} \\ &= 4 \times 10^{-6} \text{ cases/year} \end{aligned}$$

TABLE B-1. VARIABLES FOR ESTIMATING AVERAGE RISKS  
AND POPULATION RISKS

| Variable                         | Value              | Reference |
|----------------------------------|--------------------|-----------|
| Potency factor, kg-day/mg (PF)   | $1.56 \times 10^5$ | EPA 1984  |
| Absorption factor, unitless (AF) | 0.55               | EPA 1998b |

