

## **Chapter 3**

# **Environmental Considerations**

## CONTENTS

	<i>Page</i>
CHLORINATED DERIVATIVES IN THE ENVIRONMENT-AN OVERVIEW...	29
DIOXIN .....	31
DIOXIN AND PULP AND PAPER MANUFACTURE .....	32
National Dioxin Study .....	32
EPA/Paper Industry Joint Five-Mill Study .....	33
DIOXIN IN PULP AND PAPER PRODUCTS .....	35

### *Box*

	<i>Page</i>
3-A. Detection Limits and Levels of Dioxin Contamination .....	32

### *Tables*

<i>Table</i>	<i>Page</i>
3-1. Major Chlorinated Derivatives Identified in Pulp and Paper Mill Effluents .....	30
3-2. Characteristics of the Bleached Kraft Pulp and Paper Mills Used in the Five-Mill EPA/Industry Cooperative Dioxin Screening Study .....	34
3-3. Concentration of TCDD and TCDF in Bleach Plant Wastewater .....	34
3-4. Mode of Environmental Release of TCDD and TCDF From Pulp and Paper Mills .....	35
3-5. Safe-level Concentrations of TCDD in Paper Products .....	36

## Environmental Considerations

Pulp manufacture, like most chemical processes, results in emissions, effluents, and solid residues that must be disposed of. This study focuses on chlorinated bleached pulp mill waste effluents and residual chlorinated compounds in paper products (with emphasis on TCDD and TCDF), therefore air emissions and solid wastes<sup>1</sup> will not be considered here. Technologies for reducing the production of chlorinated organics in the pulping process are discussed in chapter 5.

### CHLORINATED DERIVATIVES IN THE ENVIRONMENT— AN OVERVIEW

Effluents from bleached pulp mills contain a variety of substances, some of which exhibit a variety of effects in biological tests, such as genotoxicity, mutagenicity, or teratogenicity. These include resin acids and fatty acids, chlorinated phenols, and other chlorinated organic substances. The composition of bleaching effluent is extremely complex and varies from mill to mill depending on the wood species being pulped, the pulping technology, bleaching reagents, and waste treatment systems used.<sup>2</sup> Comparatively little is known about the actual composition of mill waste effluents, although substantial scientific effort has been spent on research. A screening and verification survey of pulp and paper mill effluents conducted by the Environmental Protection Agency (EPA) tentatively identified a number of chlorinated organic chemicals (table 3-1). The chlorinated components of the waste

stream consist mostly of simple phenols, phenolic and carbohydrate oligomers (high and low molecular weight polymers), and neutral and acidic materials resulting from the breakdown of the phenolic rings in lignin.<sup>3</sup>

It has been estimated that no more than 10 percent of the total solids in the waste stream of a pulp bleaching plant contain chlorinated derivatives. However, their toxicity to aquatic biota has raised concerns among biologists.<sup>4</sup> Chlorinated mill wastes have only recently been focused on in the United States, although the toxicity of untreated, undiluted waste to aquatic biota is well documented in the scientific literature. A technical committee of Environment Ontario, the provincial environmental agency for Ontario, Canada, recently reviewed the available information on chlorinated organics and dioxin from mill waste. Based on its analysis, the committee recommended that Ontario adopt a long-term strategy aimed at completely eliminating the formation of organochlorines in kraft pulp mills.<sup>5</sup> The committee also concluded, however, that 'chlorinated dioxins do not represent an immediate danger to human health and welfare,' but it did note that heavy fish-eaters consuming fish caught downstream of some bleached kraft mills might exceed the acceptable daily intake of TCDD.

Sweden and Finland, with pulp and paper mills located adjacent to the Gulf of Bothnia and the Baltic Sea, have experienced environmental damage to marine life from chlorinated organic substances

<sup>1</sup>Solid waste disposal, particularly the disposal of contaminated sludge from biological treatment plants, is an important factor in the ultimate solution of safely disposing of dioxin. U.S. EPA information on pulp mill sludge disposal provided to OTA by Karen Florini, Environmental Defense Fund, shows that of the 104 bleached chemical pulp mills in the United States, 54 dispose of sludge in landfills, 20 use surface impoundments, 20 incinerate the sludge, 6 convert it to compost or other salable products, 6 apply it to the land as a soil amendment, and 2 dispose of it by other means (total exceeds 104 because some mills use more than one method of disposal). The subject of solid waste disposal has many aspects that range far beyond the focus of this study, including disposal of contaminated municipal sewage sludge, disposal of toxic and hazardous materials, and disposal of incinerator residues. OTA has published several reports on related topics: *Waste in Marine Environments*, OTA-O-335, April 1987; *From Pollution to Prevention: A Progress Report on Waste Reduction*, OTA-ITE-347, June 1987; *Technologies and Management Strategies for Hazardous Waste Control*, OTA-M-197, March 1983; *Serious Reduction of Hazardous Waste*, OTA-ITE-318, September 1986.

<sup>2</sup>Between 250 and 300 chemicals have been identified in pulp mill effluents. Many of these are chlorinated compounds. Leena R. Suntio, Wan Ying Shui, and Donald Mackay, "A Review of the Nature and Properties of Chemicals Present in Pulp Mill Effluents," *Chemosphere*, vol. 17, No. 7, 1988, pp. 1249-1290.

<sup>3</sup>Carlton W. Dence and Goran E. Annergren, "Chlorination," *The Bleaching of Pulp, Third Edition* (Atlanta, GA: TAPPI, 1979), p. 69.

<sup>4</sup>Ibid., p. 71.

<sup>5</sup>Environment Ontario, *Stopping Water Pollution at its Source - Kraft Mill Effluents in Ontario*, Report of the Technical Advisory Committee, Pulp and Paper Sector, Municipal/Industrial Strategy for Abatement (Toronto, Ontario: Environment Ontario, 1988), pp. 1-2.

**Table 3-1-Major Chlorinated Derivatives Identified in Pulp and Paper Mill Effluents**


---

chlorobenzene
1,1,1 Trichloroethane
trichlorophenol*
2,4-dichlorophenol
dichlorobromomethane
chlorodibromomethane
trichloroethylene
monochlorodehydroabiatic acid
2,3,7,8-tetrachlorodibenzo-p-dioxin
1,2-dichloroethane *
1,1,2,2-tetrachloroethane **
chloroform *
methylene chloride *
trichlorofluoromethane
tetrachloroethylene **
3,4,5-trichloroguaiacol
9,10-dichlorostearic acid
2,3,7,8-dibenzofurans*

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\* Listed as carcinogens in the *Fourth Annual Report on Carcinogens*, U.S. Department of Health and Human Services, Public Health Service, National Toxicology Program, 1965.

\*\* Listed as carcinogens by the National Institute of Occupational Safety and Health, sea Office of Technology Assessment, *Identifying and Regulating Carcinogens—Background Paper* (Chelsea, MI: Lewis Publishers, 1967), p. 64.

SOURCE: U.S. Environmental Protection Agency, *Development Document for Effluent Limitations Guidelines and Standards for the Pulp, Paper, and Paperboard and the Builders' Paper and Board Mills—Point Source Categories*, EPA 440/1-82/025 (Washington, DC: 1962), p. 46.

released into coastal waters.<sup>6</sup> Sweden's National Environmental Protection Board (Naturvardsverket) estimates that Scandinavian pulp and paper mills contribute between 300,000 and 400,000 tons of chlorinated organic materials to the coastal waters of Sweden, Finland, and Norway annually.<sup>7</sup> Evidence of environmental harm in the estuaries of the Baltic Sea (including the accumulation of dioxin in the flesh of food fish), where water circulation and exchange are extremely slow, has led the Swedish Government to consider regulations to reduce the amount of chlorinated organic substances produced by bleached sulfate pulp mills by imposing regulations that require the use of oxygen bleaching and increased use of chlorine dioxide bleach in place of chlorine gas. Sweden is also considering steps to

promote the use of closed-cycle processes that would significantly reduce or even eliminate the release of chlorinated wastes to the environment.

The Swedish experience, where biological waste treatment is less prevalent, contrasts with that of the United States where nearly all bleached kraft pulp mills use secondary biological treatment to reduce the biological and chemical oxygen demands of wastewater. In the course of biological treatment, many potentially toxic substances are removed and concentrated in the treatment sludge.<sup>8</sup> Many Swedish mills, on the other hand, do not use biological waste treatment, and discharge their effluent directly into the environment or use only primary waste treatment.

The overall release of chlorinated organic compounds from pulp and paper mills has received less attention in the United States up to now. Instead, the major concern arose over TCDD and TCDF that are produced along with other chlorination products during bleaching cycles and are considered to be potentially harmful to human health.<sup>9</sup> A similar pattern of concern over dioxin developed in Canada. A recent report on pollution from kraft mill effluents published by Environment Ontario warned against focusing too closely on dioxins as a result of media publicity, because it "may divert energies from productive avenues of pollution control into blind alleys of ill-conceived, routine, and expensive surveys of 'dioxin' concentrations."<sup>10</sup>

Products containing TCDD were at one time used extensively as herbicides (agent orange, 2,4,5-T). They are also produced as byproducts from the incineration of municipal and industrial waste, the combustion of wood in home furnaces, stoves, and fireplaces, metal smelters, and the incomplete combustion of dielectric fluids (PCBs) in electrical transformers. The use of dioxin-containing materials in industrial processes has since been significantly

<sup>6</sup>Committee for the Gulf of Bothnia, *Water Pollution Problems of Pulp and Paper Industries in Finland and Sweden*, Report of the Special Working Group, Naturvardsverket Rapport 3348, in English (Solna, Sweden: Baltic Marine Environment Protection Commission, 1987), app. 3.

<sup>7</sup>National Swedish Environmental Protection Board, *Action Plan for Marine Pollution* (Solna, Sweden: Naturvardsverket, 1987), p. 27.

<sup>8</sup>A well-maintained, properly operated biological Wrote treatment plant can remove 30 to 50 percent of chlorination products and about 85 percent of TCDD and TCDF that is retained on suspended solids. Preliminary, unpublished research by the industry reported at the OTA November 1988 workshop indicates that it may be possible to remove up to 90 percent of the chlorinated organics with supplemental chemical treatment. This work is still experimental.

<sup>9</sup>'Dioxins' and 'furans' refer generically to chlorinated dibenzo-para-dioxins (CDD) and chlorinated dibenzofurans (CDF), respectively, that have one to eight chlorine substituents.

<sup>10</sup>Environment Ontario, op. cit., note 5, pp.1-19.

curtailed, but their inadvertent production through chemical and industrial processes, and as combustion products continues.

## DIOXIN<sup>11</sup>

Dioxin, as generally referred to, is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). It is the most toxic of 75 chlorinated dioxins and over 135 chlorinated furans (TCDFs).<sup>12</sup> Dioxin is a byproduct of, or a contaminant in, manufactured materials. The chemical reactions and conditions under which they are formed in the pulp mill are not completely understood. TCDD was never produced as such intentionally except in small experimental quantities for research. In the United States, TCDD largely earned its reputation as a “bad actor” in the Agent Orange controversies following the use of herbicides as defoliants during the Vietnam War.

Agent Orange was a mixture of the herbicides 2,4,5-trichlorophenoxy acetic acid (2,4,5-T) and 2,4-dichlorophenoxy acetic acid (2,4-D). These same chemicals were extensively used in forestry and agriculture with little recognition of the health risks that may be related to the dioxin that 2,4,5-T contained as an incidental ingredient (2,4,5-T is no longer manufactured in the United States). The exposure of military personnel to these chemicals in Vietnam raised the consciousness of the public about the health risks of dioxins when returning veterans blamed a number of their health problems and those of their families on past exposure to Agent Orange while serving in the military.

How serious a human health threat is the exposure to dioxins? On purely scientific bases, the question of human risk has not yet been definitively answered. Epidemiological data are incomplete and difficult to interpret. No study thus far has conclusively linked dioxins to the death of a human, or to a human disease other than chloracne, or conclu-

sively related exposure to dioxin to cancer (although the carcinogenic potential is considered to be “probable”), or to miscarriages.<sup>13</sup> Abnormal behavior, genetic effects, immunological problems, enzymatic disjunctions, and reproductive problems associated with dioxin exposure have been considered, but studies have not confirmed dioxins to be the cause.

With regard to certain-but not all—laboratory test animals, dioxin has been shown to be extremely toxic and lethal at low levels. Procedures for extrapolating from animal effects to humans are controversial. There is, however, sufficient scientific evidence to suggest that human exposure to dioxin should be minimized within acceptable levels of risk pending a better understanding of its health implications. The public perceives dioxins to be dangerous and a major health risk as a result of publicity surrounding the Agent Orange controversy, the Times Beach incident, the Love Canal, and problems related to the disposal of hazardous wastes. The regulatory agencies have opted for a conservative approach to regulating dioxins.

Research on rainbow trout, a species often used to gauge the toxicity of chemicals, suggests that TCDD and TCDF can cause mortality, reduced growth, and abnormal behavior during the fishes’ early life stages. TCDD was judged to be 10,000 times more toxic than the pesticides endrin or toxaphene, while TCDF was 1,000 times more toxic.<sup>14</sup> Bioconcentration factors (BCF) for TCDD were found to be much higher than originally estimated. TCDD accumulated to about 39,000 times the ambient concentration of the water, and TCDF between 2,640 and 4,449 times (but dioxin seems to concentrate in the gut and inedible parts of fish). It has also been shown that similar preferential bioaccumulation or magnification of TCDD and TCDF occurs in aquatic birds.<sup>15</sup> However, the effects of TCDD and TCDF on

<sup>11</sup>This discussion of the human health effects of dioxin is not intended to be definitive or analytical with regard to the dangers of dioxin. Rather, it is an encapsulation of other recent surveys of existing knowledge about dioxin and its congeners.

<sup>12</sup>Tests on laboratory animals suggest that if the toxicity of 2,3,7,8-TCDD is assigned the value of 1.0, the toxicity of 2,3,7,8-TCDF is 0.1. Other dioxins and furans also generally have toxicities that are estimated to range from one-tenth to one-thousandth that of 2,3,7,8-TCDD.

<sup>13</sup>U.S. Environmental Protection Agency, *National Dioxin Study*, EPA/530-SW-87-025 (Washington, DC: 1987), pp. 1-8.

<sup>14</sup>Paul M. Mehrle et al., “Toxicity and Bioconcentration of 2,3,7,8-Tetrachlorodibenzodioxin and 2,3,7,8-Tetrachlorodibenzofuran in Rainbow Trout,” *Environmental Toxicology and Chemistry*, vol. 6, 1988, pp. 47-62.

<sup>15</sup>D.L. Stalling et al., “Patterns of PCDD, PCDF, and PCB Contamination in Great Lake Fish and Birds and Their Characterization by Principal Component Analysis,” *Chemosphere*, vol. 14, No. 6/7, 1985, pp. 627-643.

reproduction, survival, and behavior of bird populations is uncertain.<sup>16</sup>

## DIOXIN AND PULP AND PAPER MANUFACTURE

### *National Dioxin Study*

The National Dioxin Study (NDS), a 2-year effort to explore the extent of dioxin contamination in the environment, detected the presence of TCDD and TCDF in fish and bottom sediment samples collected downstream of several U.S. pulp mills.<sup>17</sup> Fish samples for the NDS were selected in three ways:

- 90 sites were selected statistically,
- . 305 sites near urban and industrial areas were nominated by EPA's Regional Offices or the Office of Water Regulations and Standards (OWRS), and
- . 57 estuarine or coastal sites were sampled.

Of the 90 sites sampled statistically for fish contamination, 17 showed detectable levels of TCDD up to 19 parts per trillion (ppt) in composite whole fish samples (see box 3-A). Nearly one-third of the 305 regional samples showed detectable levels of dioxin in whole fish samples. These sample sites included rivers, lakes, and some coastal and estuarine waters. TCDD levels in some samples ranged up to 85 ppt. Only 4 of the 57 estuarine and coastal sites sampled had detectable levels of dioxin in fin fish or shellfish, and these ranged between 1.08 and 3.5 ppt.

About 80 percent of the whole fish sampled from sites in the Great Lakes were found to have detectable levels of dioxin. A multitude of potential dioxin sources are within the watershed of the Great Lakes and the turnover and flushing of the waters within the Lakes are extremely slow. Outside the Great Lakes, detectable dioxin levels were most frequently found in the major river systems that flow through industrial and urban areas. Advisories have been issued by Wisconsin, Maine, and Louisiana warning of possible risk of eating contaminated fish.

### **Box 3-A—Detection Limits and Levels of Dioxin Contamination**

Determining the amount of dioxin in the natural environment requires sophisticated analytical procedures and careful statistical sampling and sample preparation. High resolution gas chromatography and mass spectrometry are used to quantify dioxin levels. Gas chromatography separates the dioxins from other compounds by selectively adsorbing the dioxins (based on their specific molecular weights) on an adsorbent such as activated charcoal, alumina, or silica gel. Mass spectrometry separates the dioxins specifically and quantitatively according to their atomic weights. These technologies can measure dioxins in the range of parts per quadrillion (Ppq) in water samples, but this level of detection is still considered experimental for most biological samples.

EPA selected a nominal detection limit of one part per trillion (ppt) for fish and soil samples collected in the course of the National Dioxin Study. This sensitivity pushed the limits of the state-of-the-art in analytical technology. Comprehending parts per quadrillion and parts per trillion cart boggle the mind. One ppt is equivalent to 1 second in 32,000 years. One ppq is equivalent to 1 second in 32,000,000 years. The potency of dioxin makes measurements at this minute level of resolution important.

The Food and Drug Administration (FDA) recommends that consumption of fish be limited if dioxin content exceeds 25 ppt, and consumption is banned when levels reach 51 ppt. In general, EPA found that dioxin levels of fish fillets—the edible portions of the fish—had dioxin levels below the detection limits even though whole fish samples may be judged to be contaminated.

At two-thirds of the sites where dioxin was detected, the maximum values encountered were below 5 ppt. At only four sites did dioxin levels exceed 25 ppt (the level at which FDA recommends that fish consumption be limited). The high-level sites were located in the Androscoggin River at Lewiston, Maine (29 ppt), and the Rainy River at

<sup>16</sup>J.E. Elliot et al., "Levels of Polychlorinated Dibenzodioxins and Polychlorinated Dibenzofurans in Eggs of Great Blue Herons (*Ardea herodias*) in British Columbia, 1983-1987: Possible Impacts on Reproductive Success," Progress Notes No. 176, Canadian Wildlife Service, April 1988, p. 7.

<sup>17</sup>U.S. Environmental Protection Agency, *National Dioxin Study*, EPA/530-sw-87-025 (Washington, DC: 1987), pp. III-32-33.

<sup>18</sup>Ibid., pp. III-29.

International Falls, Minnesota (85 ppt), both of which are located downstream of pulp and paper mills.<sup>19</sup> Additional investigations at these sites showed dioxin levels of up to 414 ppt in waste treatment sludges from the mills.

As a follow-on to the NDS, EPA is investigating other chemical pollutants that might accumulate in fish. The National Bioaccumulation Study (NBS), which is currently underway, is focusing on a subset of “priority” pollutants selected from among 400 potential chemicals. These include non-conventional pesticides, semi-volatile organic chemicals known to accumulate in human fatty tissue, agricultural chemicals, industrial chemicals, and those in pulp mill effluents. Four hundred sites are being sampled in targeted industrial, urban, and agricultural areas and below pulp mills. Approximately 95 percent of the fish samples have been collected. Of the 75 samples that have been analyzed from fish collected below pulp mills, 67 are reported to have dioxin above detectable levels. Samples from 10 mill sites report TCDD and TCDF concentrations in fish fillet tissue above the acceptable FDA limits of 25 ppt.<sup>20</sup>

Recent data from the NBS based on fish sampled from 18 southern rivers receiving mill wastes showed accumulations of dioxin in whole fish ranging from about 1 ppt up to 164 ppt. Most whole fish samples had dioxin levels between 10 and 40 ppt. Three whole fish samples had levels exceeding 100 ppt. The edible part of the fish (fillets) contained much lower dioxin levels and none exceeded FDA’s 25 ppt acceptable limits, although one fish showed a level of 24 ppt of dioxin.<sup>21</sup>

### ***EPA/Paper Industry Joint Five-Mill Study***

*The* results of the National Dioxin Study indicated that effluent from the manufacture of pulp can introduce detectable levels of dioxin into the environment. This prompted the U.S. pulp and paper

industry, through the National Council of the Paper Industry for Air and Stream Improvement, and EPA to undertake a joint investigation of five bleached kraft pulp and paper mills in 1986.<sup>22</sup> The cooperative screening study focused on three mills known to have dioxin in their waste sludge (all of the mills sampled used the activated sludge waste treatment process) plus two additional mills that were volunteered by their firms to provide broader geographical coverage (table 3-2). The results of the cooperative five-mill study indicated that the bleaching of kraft pulp with chlorine and chlorine derivatives is responsible for the formation of 2,3,7,8 -TCDD and 2,3,7,8 -TCDF as byproducts of the pulping process.

### **Dioxin in Bleached Pulps**

Sensitive gas chromatographic procedures were used to distinguish between the amounts of 2,3,7,8-TCDD and the related isomers of chlorinated furan (2,3,7,8-TCDF) in the bleached pulp and mill wastes. TCDD was detected in seven of nine bleached pulps sampled, at levels up to 51 ppt. The median TCDD content was 4.9 ppt, and the mean was 13 ppt.<sup>23</sup> TCDF was found in eight of nine pulp samples at levels ranging from below detection limits to 330 ppt. The median TCDF content was 50 ppt, and the mean was 93 ppt.

### **Dioxin in Bleach Plant Wastewaters**

Wastewater from each stage of the pulp bleach sequence was systematically sampled at each mill. TCDD was detected in wastewaters at three of the five mills, and TCDF was detected at four of the five mills sampled. The greatest discharge of both TCDD and TCDF was associated with the caustic extraction stage, which serves to flush away the lignin and other coloring agents that are mobilized during the bleaching stages. Lesser amounts of TCDD and TCDF were detected in the wastewaters of the hypochlorite bleaching stage and the chlorination bleaching stages (see table 3-3).

<sup>19</sup>*Ibid.*, pp. 111-30.

<sup>20</sup>Steven Croner, U.S. Environmental Protection Agency, unpublished materials presented at OTA dioxin workshop, Washington, DC, Nov. 14-15, 1988.

<sup>21</sup>National Bioaccumulation Study data provided to OTA by Karen Florini, Environmental Defense Fund, Washington, DC, Feb. 6, 1989.

<sup>22</sup>G. Amendola et al., “The Occurrence and Fate of PCDDS and PCDFs in Five Bleached Kraft Pulp and Paper Mills,” presented at the Seventh International Symposium on Chlorinated Dioxins and Related Compounds, Las Vegas, NV, October 1987.

<sup>23</sup>*Ibid.*, p. 8.

**Table 3-2—Characteristics of the Bleached Kraft Pulp and Paper Mills Used in the Five-Mill EPA/industry Cooperative Dioxin Screening Study**

Mill	Furnish (in percent)		Daily capacity (tons)	Bleach sequences		Daily effluent production (million gallons)
	Hardwood	softwood		Hardwood	softwood	
I	85	15	500	CE <sub>2</sub> H & CE <sub>2</sub> HHP	CE <sub>2</sub> HHP	23
II	20		775 <sup>a</sup>	CEHD	CEHD	36
III	100	NA	1,000	C/DEoD		36
IV	NA	100	400 <sup>b</sup>	—	CEH <sup>-</sup>	18
V	30	70	1,200 <sup>c</sup>	CdE <sub>2</sub> H/D	CdE <sub>2</sub> H/D	41

NA = Not applicable

<sup>a</sup> C also produce 300 tons per day of refiner mechanical groundwood pulp.

<sup>b</sup> Has additional capacity to produce 830 tons per day of groundwood.

<sup>c</sup> Also can produce 130 tons of groundwood daily.

SOURCE: G. Amendola et al., "The Occurrence and Fate of PCDDs and PCDFs in Five Bleached Kraft Pulp and Paper Mills," paper presented at the Seventh International Symposium on Chlorinated Dioxins and Related Compounds, Las Vegas, NV, October 1987.

**Table 3-3—Concentration of TCDD and TCDF in Bleach Plant Wastewater**

Bleaching stage	TCDD (ppt)			TCDF (ppt)		
	Range	Median	Mean	Range	Median	Mean
Chlorination	0.01-0.24	0.04	0.07	0.06-3.8	0.24	0.65
Caustic wash	0.01-3.6	0.24	1.00	0.06-33.0	0.78	7.4
Hypochlorite	0.02-1.9	0.20	0.40	0.09-9.2	0.59	2.3
Chlorine dioxide	0.01-0.03	ND	ND	0.01-0.13	ND	ND

ND= Not detectable

SOURCE: G. Amendola et al., "The Occurrence and Fate of PCDDs and PCDFs in Five Bleached Kraft Pulp and Paper Mills," paper presented at the Seventh International Symposium on Chlorinated Dioxins and Related Compounds, Las Vegas, NV, October 1987.

### Dioxin in Wastewaters and Sludges

Comparisons among the mills indicated that the TCDD and TCDF contents of pulp and wastewater differed greatly from mill to mill. TCDD produced in the pulp bleaching process can be transported to the environment as a residual in finished pulp, in the sludge recovered in the wastewater treatment process, or as treated effluent released into streams and pond (table 3-4). TCDD was found in wastewater treatment sludges at each of the five mills sampled.<sup>24</sup> Analyses of wastewater from the paper machines showed that some of the dioxin produced in the bleaching process was passed through to the paper making process.

### Continuing Efforts

Although the five-mill cooperative survey confirmed that chlorinated bleaches can produce dioxins in the manufacture of bleached wood pulp, the

study revealed great variability in dioxin concentrations among the mills and within the pulps, waste sludge, and treated effluents. The results demonstrated the need for a comprehensive and systematic survey of the receiving waters and biota below the waste outlets of U.S. pulp mills in order to better understand the scope and intensity of the environmental loading of TCDD. The survey also indicated that more detailed information was needed about dioxin levels at various steps in the pulping process and in the bleaching sequence.

EPA has recently negotiated a cooperative agreement with the American Paper Institute (API) and the National Council of the Pulp and Paper Industry for Air and Stream Improvement (NCASI), both associated with the U.S. pulp and paper industry, to survey all 104 domestic pulp mills that manufacture chemical bleached pulp for production of dioxin and

<sup>24</sup>U.S. Environmental Protection Agency, *U.S. EPA/Paper Industry Cooperative Dioxin Screening Study*, EPA-440/1-88-025 (Washington, DC: 1988), p. viii.



**Table 3-4-Mode of Environmental Release of TCDD and TCDF From Pulp and Paper Mills (percent)**

Source	Mill				
	I	II	III	IV	V
<b>2,3,7,8-TCDD</b>					
Bleached pulp .....	19	66	—	30	57
Waste sludge .....	16	16	100	70	22
Treated effluent .....	65	18	—	—	21
<b>2,3,7,8-TCDF</b>					
Bleached pulp .....	19	56	60	31	55
Waste sludge .....	17	<b>20</b>	<b>36</b>	<b>69</b>	22
Treated effluent .....	64	24	4	—	23

SOURCE: G. Amendola et al., "The occurrence and Fate of PCDDs and PCDFs in Five Bleached Kraft Pulp and Paper Mills," paper presented at the Seventh International Symposium on Chlorinated Dioxins and Related Compounds, Las Vegas, NV, October 1987.

furan isomers.<sup>25</sup> In addition, an industry study will undertake a detailed analysis of dioxin levels and bleaching processes at selected pulp mills.

The study will consider the full range of factors that might affect the production and dispersal of dioxins, including annual effluent flow, wastewater treatment, sludge disposal practices, bleach plant operations, and an analysis of dioxin contents of effluents, pulps, and sludges. Detailed analyses of dioxin levels in 25 bleach lines will be included. The study began in the summer of 1988, and is expected to be completed in the summer of 1989.

In a related effort, an EPA-led interagency group has undertaken a Multi-Media Risk Study that will utilize data collected in the EPA/Industry 104-mill study. Under a court-approved consent agreement to consider dioxin in paper, EPA is attempting to estimate the cumulative risk of dioxin from this source in all media—pulp, sludge, and effluent.<sup>26</sup> Data collected in the 104-mill study, and estimates of migration rates of TCDD and TCDF from paper products adjusted by product-use scenarios, will be used to determine whether or not there is a human risk from dioxin in pulp and paper.<sup>27</sup> The consent decree also requires EPA to undertake an assessment of environmental risks as well as human risks. The Food and Drug Administration (FDA) and Con-

sumer Safety Product Commission (CSPC) have initiated product risk assessments that will become part of the interagency multi-media study.

## DIOXIN IN PULP AND PAPER PRODUCTS

The finding of TCDD and TCDF in bleached pulp samples raised questions as to whether residual TCDD might also find its way into finished paper products and present a potential health risk to consumers through dermal contact (it did not consider other routes of exposure). The NCASI commissioned Envirologic Data, Inc. to assess the potential risks<sup>28</sup> to human health from skin exposure to a variety of bleached pulp products, including disposable diapers, facial tissue, toilet tissue, sanitary napkins, and paper towels.<sup>29</sup>

The results of Envirologic Data's risk assessment of concentrations of TCDD found in paper products were related to a lifetime cancer risk of one in a million in the general population—a regulatory standard commonly used by the EPA and the FDA to gauge risk. Based on this measure of risk, a "virtually safe concentration" of TCDD equivalents was calculated for the various products tested (table 3-5).

<sup>25</sup>See *Federal Register*, vol. 53, No. 27, Feb. 10, 1988, p. 3937; EPA Office of Water Regulations and Standards, and office of Toxic Substances, U.S. EPA/Paper Industry Cooperative Dioxin Study—Tier 1, Fact Sheet, Feb. 4, 1988.

<sup>26</sup>See, *Environmental Defense Fund & National Wildlife Federation v. Thomas*, No. 85-0973 (D. D. C., consent decree entered July 27, 1988).

<sup>27</sup>Dwain Winter, U.S. Environmental Protection Agency, communication at the OTA dioxin workshop, Washington, DC, Nov. 14-15, 1988.

<sup>28</sup>Risk assessment is the characterization of the probability of potentially adverse health effects from human exposure to environmental hazards. The risk assessment process consists of four steps: 1) hazard identification, 2) dose-response assessment, 3) exposure assessment, and 4) risk characterization. NCASI used EPA's guidelines for Carcinogen Risk Assessment as a framework for the dioxin dermal exposure study.

<sup>29</sup>National Council of the Paper Industry for Air and Stream Improvement, *Assessment of Potential Health Risks From Dermal Exposure to Dioxin in Paper Products*, Technical Bulletin No. 534 (New York, NY: 1987), p. 107.

Table 3-5—Safe-level Concentrations of TCDD in Paper Products

	Calculated TCDD equivalent (in ppt)		Measured
	Female	Male	
Bleached pulps .....			5 <sup>a</sup>
Communication paper .....			13 <sup>b</sup>
Clerical worker .....	9,000	9,100	
Manager .....	4,200	4,300	
Personal care products			
Disposable diapers .....			0 <sup>c</sup>
Conventional .....	<b>540,000</b>	<b>540,000</b>	
Superabsorbent .....	2,000,000	2,000,000	
Facial tissue			
Normal use .....	66,000,000	79,000,000	
Makeup .....	230,000		
Toilet tissue .....	27,000,000	65,000,000	
Sanitary pads .....	63,000,000		
Paper towels .....	<b>7,900,000</b>	<b>9,500,000</b>	
Composite personal care products <sup>d</sup> .....	160,000	510,000	
Combined communication papers and personal care products .....			4
Clerical worker .....	8,500	8,900	
Manager .....	4,100	4,200	

<sup>a</sup> Measured in 7 pulps with levels of dioxin from less than 1 ppt to 51 ppt, with a median of 4.9 ppt.

<sup>b</sup> Measured in bond paper.

<sup>c</sup> No TCDD detected in disposable diapers at detection limits of 2.1 and 2.6 ppt.

<sup>d</sup> Excluding superabsorbent disposable diapers.

SOURCE: National Council of the Paper Industry for Air and Stream Improvement, *Assessment of Potential Health Risks From Dermal Exposure to Dioxin in Paper Products*, Technical Bulletin No. 534 (New York, NY:1987), p 107.

Calculated safe levels for bond paper, newspaper, and other paper used for communications ranged from 4,200 ppt of TCDD for female managers to 9,100 ppt for male clerks. Safe levels for personal care products were calculated to range from 230,000 ppt of TCDD for female facial tissue used for makeup removal to 79,000,000 ppt for facial tissue by males. Safe levels for paper towels were calculated at 7,900,000 ppt for females and 9,500,000 ppt for males. Toilet tissue safe limits for females were calculated at 27,000,000 ppt for females and 65,000,000 ppt for males. Actual concentrations of TCDD in samples of bond paper were determined to be about 13 ppt: in paper towels, 4 ppt: and no detectable TCDD was measured in disposable diapers.

NCASI published the results of an assessment of potential exposure to dioxin from coffee brewed using bleached coffee filters in May 1988.<sup>30</sup> Based on an assumed consumption profile for an average and heavy coffee drinker and assuming that 65 to 90

percent of the dioxin migrated from the filter, NCASI concluded that the calculated dioxin TEQs for a risk ranging from zero to one in one-million to be between 20 ppt TCDD TEQs for average coffee drinkers to 11 ppt TCDD TEQs for heavy coffee drinkers. The coffee filters tested had TEQ dioxin contents ranging from 2.2 to 6.6 ppt.

An assessment of dioxin in food packaging paper products has been initiated.<sup>31</sup> NCASI commissioned ENVIRON, Inc. to undertake the evaluation. A number of food contact products are scheduled to be undergo risk assessment, such as paper cups and plates, convenience food packaging, paper towels, and pizza boxes. NCASI has put the project on hold pending the development of acceptable test procedures to determine the absorption of dioxin into fatty foods. The assessment will resume when test protocols are developed

Scientists at Health & Welfare Canada, a government agency, reported in August 1988 that they had

<sup>30</sup>National Council of the Paper Industry for Air and Stream Improvement, *Assessment of the Risks Associated With Potential Exposure to Dioxin Through the Consumption of Coffee Brewed Using Bleached Paper Coffee Filters*, Technical Bulletin 546 (New York, NY: 1988), p. 34.

<sup>31</sup>National Council of the Paper Industry for Air and Stream Improvement, *First Progress Report on the Assessment Of Potential Health Risks From Use of Bleached Board and Paper Food Packaging and Food Contact Products*, Special Report 87-11 (New York, NY: 1987), p. 27.

detected 0.04 ppt of TCDD and 0.75 ppt of TCDF in whole milk packaged in plasticized bleached paper cartons. They r<sup>epoted</sup> no similar level in milk

packaged in non-bleached paper containers. NCASI is currently collaborating with Canadian scientists to confirm these findings.

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<sup>32</sup>John J. Ryan, Food Research Division, Health Protection Branch, Health & Welfare Canada, Ottawa, Canada, paper presented at the International Dioxin Symposium, Umca, Sweden, August 1988.