PAPER TASK FORCE

*Duke University ** Environmental Defense Fund*
*Johnson & Johnson ** McDonald's*
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WHITE PAPER NO. 5

ENVIRONMENTAL COMPARISON OF BLEACHED KRAFT PULP MANUFACTURING TECHNOLOGIES

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TABLE OF CONTENTS

LIST OF TABLES AND FIGURES

I. INTRODUCTION

This paper summarizes the research and findings of the Paper Task Force on an environmental comparison of bleached kraft pulp manufacturing processes. This paper is one element of an extensive research process in support of the task force's work to develop recommendations for purchasing "environmentally preferable paper", paper that reduces environmental impacts while meeting business needs.

The information presented in this paper has come from a range of sources including articles in peer reviewed journals, the trade press, conference proceedings, reports of studies commissioned by the pulp and paper industry, relevant documents from the U.S. Environmental Protection Agency (EPA), information gathered during Paper Task Force technical visits and presentations from experts.

As one step in the research process, on September 21, 1994 the Task Force assembled a panel of experts to discuss an environmental comparison of bleached kraft pulp manufacturing technologies. In preparation for this panel, the task force prepared an "issue paper" that examined relevant issues and a range of perspectives. The panelists addressed topics discussed in this paper during the panel. The issue paper was also reviewed by several expert reviewers from companies and institutions not represented on the panel. The panelists' and reviewers' comments on the issue paper have been considered in drafting this White Paper. A draft of this paper also was reviewed by experts in pulp and paper manufacturing from industry and the environmental community. Appendix A contains a list of the panelists and reviewers of the issue paper and the draft of white paper.

The Paper Task Force members endorse the broad principles set forth by the Task Force's final report. The findings and research in this White Paper reflects the contribution of Paper Task Force Working Groups and changes made in response to comments received from expert reviewers through the White Paper review process. The contents of this paper do not reflect the policy of individual Task Force member organizations.

The research presented in this paper is one element of the *environmental* analysis being performed by the task force. Other White Papers address economic and functional issues relevant to the manufacture of paper. We present a complete list of the White Papers at the beginning of the appendices.

A. An Overview of the Bleached Kraft Pulp Manufacturing Process

The task force decided to study the environmental issues associated with the use of different bleached kraft pulp manufacturing technologies because bleached kraft pulp is the dominant high quality bleached pulp in both the U.S. and the world. 98% of bleached chemical pulp capacity in the United States and 93% worldwide use the kraft process.[1] When comparing different manufacturing processes, we do not focus solely on the bleach plant. Developments in extended delignification and oxygen delignification, aspects of the pulping process, also must be considered in any discussion of bleached kraft pulp manufacturing.

1. Pulping

To produce high quality pulp from wood, the desired cellulose fibers are chemically separated from the rest of the wood, especially from a complex organic "glue" known as lignin. Most of the lignin is removed during the pulping process where wood chips, chemicals and steam react in a pressurized vessel known as a digester. After two to four hours in the digester, the pulp is washed to remove the black liquor, a mixture of degraded lignin, other wood components and used pulping chemicals. The dark brown product, unbleached kraft pulp, consists of long, strong fibers that are ideal for grocery bags and corrugated shipping containers. The pulp is stored for future use, while the black liquor is concentrated and sent to a special furnace called the recovery boiler. In the recovery boiler, the organic waste is burned, producing steam and electricity for mill operations, and the pulping chemicals are recovered for reuse within the mill. Trace amounts of organic sulfur compounds formed during the pulping process cause the "rotten eggs" smell that has been associated with kraft pulp mills.

2. Bleaching

Mills that use conventional digesters remove 90-95% of the lignin during the pulping process; more selective bleaching agents then remove the remaining lignin and colored substances to brighten the brown unbleached pulp to a white pulp. Kraft pulp bleaching processes consist of several stages to minimize chemical use and to maintain the strength of the pulp. The pulp usually is washed after each bleaching stage to remove any organic material that can be washed out with water.

The first stages in the bleaching process remove most of remaining lignin in the unbleached pulp; the last stages brighten the pulp. In the first bleaching stage, the pulp is exposed to oxidants which break down the lignin polymer and make it more reactive with other bleaching chemicals. Chlorine, an inexpensive and powerful bleaching agent, and small amounts of chlorine dioxide, a powerful oxidizing agent that selectively attacks the lignin, traditionally have been used in this stage.

In the next stage of the bleaching process, the pulp is exposed to a solution of caustic (sodium hydroxide). In this stage, known as alkali extraction, the caustic reacts with the degraded lignin so that it dissolves in water and can be washed out of the pulp. Because most of the remaining lignin is removed from the pulp in this stage, the extraction stage is the main source of color and organic material in the effluent. In the final stages, chlorine dioxide, sodium hypochlorite or hydrogen peroxide may be used to brighten the pulp. In traditional bleaching processes, relatively little organic waste is generated during these last stages.

At all but one U.S. bleached kraft mills, this wastewater or effluent from the bleach plant, along with effluent from other parts of the mill, undergo primary and secondary treatment before being discharged into the receiving water.[2] By the end of 1995, all Canadian mills will have secondary treatment systems in order to meet new environmental regulations. All of the bleached kraft mills in Finland have secondary treatment.[3] Eight of the fifteen Swedish bleached kraft mills have secondary treatment; however, the Swedish mills chose a different strategy to control water pollution. These mills installed oxygen delignification rather than treat the pollution created by the manufacturing process. To meet the target levels proposed by the Swedish EPA, several mills plan to "close-up" their bleach plants. For mills that lack secondary treatment, the measures to minimize bleach plant effluent flow may be combined with a compact secondary treatment system if necessary to meet the target levels.

3. New Technologies

The mill's bleaching process generates most of the organic waste discharged in the effluent of a bleached kraft mill. Most mills discharge this effluent after secondary treatment because residual chlorides make the effluent too corrosive to be sent to the chemical recovery system. Mills often operate the first bleaching stage with chlorine and chlorine dioxide at low consistency (3-5% pulp in water); thus, limited evaporation capacity and increased energy requirements to recirculate this water to the recovery boiler may make reuse impractical. The effluent from the bleaching process is combined with other mill effluents, treated and discharged into the mill's receiving water, usually a river or lake. Mills can reduce the amount of organic waste they discharge to the river by removing as much lignin as possible before the pulp is exposed to bleaching chemicals.

Advances in pulping and bleaching technologies now make it possible for mills to produce a bright, strong pulp and also open the door to reusing the water (filtrates) from the bleaching process. Several equipment companies have developed digesters that can extend the cooking process -- they can remove more lignin while maintaining pulp strength. Mills also use anthraquinone in the digester to increase delignification while maintaining pulp strength.[4] More mills are using oxygen based chemicals, e.g., oxygen, ozone and hydrogen peroxide, in their bleaching processes. These chemicals also react with the residual lignin in the pulp, but in slightly different ways than do the chlorine-based chemicals.[5] Because engineers have a better understanding of how to protect the cellulose from the degradation that can occur in the bleaching process, the use of these chemicals has increased.

The oxygen-based chemicals do not produce corrosive chlorides when used in the bleaching process, so the bleach plant filtrate is more amenable to recirculation to the chemical recovery system. A considerable effort is underway to better understand how to develop "effluent-free" bleach plants based on totally chlorine-free (TCF) and elemental chlorine-free (ECF) technologies. Mills with TCF bleaching sequences would recirculate all of the bleach plant filtrate to the chemical recovery system. The organic material would be burned in the recovery boiler, while the non-process inorganic material would be removed from the system with different chemical recovery system solid wastes. Mills that operate "effluent-free" bleach plant with ECF bleaching sequences would recover the water from the acidic bleach plant filtrate and dispose of the chlorinated organic and inorganic compounds that remain. Engineering firms are currently developing technologies to concentrate the filtrate using evaporation and then incinerate the residue. The extraction stage effluents that contain chlorinated organic compounds will, at a minimum, load the recovery cycle with chlorides that will have to be purged in some fashion.

As mills eliminate the use of elemental chlorine in the bleaching process, they can choose from many technologies. The technologies considered in depth in this paper require a significant capital investment. Cutting edge technologies such as enzymes and peracids may offer lower capital cost options, but with increased operating costs, to reduce elemental chlorine and chlorine dioxide use.[6] however, these processes currently require additional laboratory and pilot-scale development before they will become commercially viable.

B. Major Topics

Sustainable manufacturing processes minimize the consumption of natural resources and minimize the quantity of the releases to the environment while maximizing their quality. Thus, to examine the sustainability of bleached kraft pulp manufacturing technologies, we present a comparison of the magnitude of the energy consumption and environmental releases associated with these technologies.. Energy consumption includes the energy required to produce the bleaching chemicals off-site. Environmental releases include air emissions from non-combustion process sources, wastewater discharge and solid waste generation. On average, reducing the magnitude of energy consumption and environmental releases reduces the potential environmental impacts associated with bleached kraft pulp production; however, because most of the releases considered in this paper have local environmental effects, *their impact on the environment will vary with the receiving environments of individual mills.* In other words, because mills have different receiving environments, the same level of emissions may have adverse effects in some cases and not in others.

In this paper, we compare ECF, and low-effluent ECF and TCF bleached kraft pulp manufacturing technologies to a base case mill that uses traditional pulping and 50% chlorine dioxide and 50% elemental chlorine in the first bleaching stage. A description of the technology options and a brief discussion of current levels of their use follows. We present abbreviations used herein to describe the pulping and bleaching processes in **Table 1**.

Table 1. Abbreviations for pulping and bleaching processes

Symbol	Pulping or bleaching process
C	Elemental chlorine
D	Chlorine dioxide
E	Alkali extraction
(EO)	Alkali extraction reinforced with oxygen
(EP)	Alkali extraction reinforced with hydrogen peroxide
(EOP)	Alkali extraction reinforced with oxygen and hydrogen peroxide
ED	Extended delignification[7]
H	Sodium hypochlorite
O	Oxygen
P	Hydrogen Peroxide
Q	Chelating stage (removes metals)
S	Sodium meta-bisulfite (a reducing agent that destroys residual hydrogen peroxide)
Z	Ozone

1. Base case

We assume that the base case mill bleaches pulp produced in a traditional digester with 50% chlorine dioxide substitution in the first bleaching stage in a four or a five stage bleaching process. 50% chlorine dioxide substitution represents the mid-point between those mills that have added oxygen and hydrogen peroxide to the alkaline extraction stages to increase the chlorine dioxide substitution to about 30% in the first bleaching stage and mills that have invested in additional chlorine dioxide capacity to achieve chlorine dioxide substitution levels of 70-100%.

2. Traditional ECF Bleaching

To move from the base case to this option, a mill replaces all of the elemental chlorine in the first bleaching stage with chlorine dioxide. This mill uses a conventional digester to produce the pulp, so the amount of lignin in the unbleached pulp before it enters the bleach plant is the same as that of the base case. The first alkali extraction stage of a five-stage bleaching process is often reinforced with oxygen and/or hydrogen peroxide to minimize the use of chlorine dioxide. This process is abbreviated as D(EOP)DED.

Mills that use some older chlorine dioxide generation technologies do not produce purely ECF pulp because these generators produce as much as 0.6 metric tons of elemental chlorine per metric ton of chlorine dioxide. The newer chlorine dioxide generation technologies have reduced the amount of by-product elemental chlorine to 0.02 metric tons or less per metric ton of chlorine dioxide.[8]

Mills must carefully balance the quantity of chlorine dioxide, with the pH, temperature and time in the bleaching tower to maximize delignification and avoid side reactions that can reduce delignification efficiency, reduce pulp strength or increase the formation of chlorinated organic substances. Without careful process control, as much as 40% of the chlorine dioxide may be converted into elemental chlorine during the delignification process.[9] Elemental chlorine reacts almost instantaneously with the aromatic rings on the lignin to generate chlorinated phenolic compounds and chloride ions;[10] thus, the elemental chlorine generated during the reaction can form the highly chlorinated AOX that may be associated with ECF bleaching. With good mixing to maintain low concentrations of elemental chlorine and low temperatures, mills can minimize the formation of highly chlorinated compounds. Bleaching vessel retention time also must be carefully controlled. As the reaction time and the concentration of elemental chlorine increase, more highly chlorinated dissolved, chlorinated lignin fragments can form.

3. Enhanced ECF Bleaching

In this option mills reduce the amount of lignin (i.e., lower the Kappa number of the pulp, a measure of lignin content) in the unbleached pulp using extended delignification and/or oxygen delignification (O). We use the term “enhanced” to describe the manufacturing processes that include these technologies. The unbleached pulp then undergoes ECF bleaching. Most mills that use this technology option reinforce the alkali extraction stage with oxygen.

4. Low-effluent and Effluent-free ECF and TCF Bleach Plants

This option focuses on ECF and TCF bleaching technologies that allow the bleach plant filtrate to be reused in the manufacturing process. Low-effluent ECF and TCF bleaching sequences build upon enhanced delignification to recirculate the filtrate from several bleaching stages, including the first alkaline extraction stage, back to the chemical recovery system where the organic waste is burned in the recovery boiler to generate energy. These mills discharge the filtrate from the final bleaching stage. In theory, effluent-free mills reuse all of the bleach plant filtrate. We will discuss the current research on effluent-free systems in this section. The analysis of energy consumption and environmental releases will focus on low-effluent ECF and TCF bleaching processes because mills use these technologies today; whereas no mills are operating in an effluent-free mode, as yet.

a) Low-Effluent ECF Processes

We consider two low-effluent ECF sequences, one is currently used at several mills worldwide, and the other will undergo a mill scale demonstration in 1996. In the first low-effluent ECF sequence, mills replace the first chlorine dioxide bleaching stage with ozone, as Union Camp has done at one of the three fiber lines at its Franklin, VA mill. In the second low-effluent ECF sequence, mills may be able to modify the chemical recovery system to allow for the recycling of filtrate from a bleach plant that uses chlorine dioxide in the first stage as Champion proposes with the experimental Bleached Filtrate Recycling (BFR™) technology.[11]

b) Low-Effluent TCF Processes

TCF bleaching processes use a combination of oxygen, ozone, hydrogen peroxide and other chemicals that do not contain chlorine. Mills minimize the amount of lignin in the unbleached pulp to produce high quality TCF pulp; as a result, all TCF manufacturing processes require enhanced delignification, either with extended delignification and oxygen delignification at modern mills or with oxygen delignification and anthraquinone. Louisiana-Pacific adds anthraquinone to the digester and uses oxygen delignification followed by three hydrogen peroxide bleaching stages to produce 85 GE brightness softwood TCF pulp.[12] Södra Cell currently uses a combination of extended delignification, oxygen delignification and hydrogen peroxide to produce full brightness (≥ 88% ISO) softwood kraft pulp at its Värö, Sweden mill, and an ozone TCF process to produce full brightness hardwood bleached kraft pulp at the Mönsterås, Sweden mill.[13] Mills with TCF processes can recirculate some, and may be able to recirculate all, of their bleach plant filtrate to the chemical recovery system.

c) Effluent-Free ECF and TCF Processes

Once mills recirculate the bleach plant filtrate from the first bleaching and alkaline extraction stages, the next step involves recirculating all of the filtrate in an effluent-free bleach plant. No mill currently operates an effluent-free bleach plant,[14] but engineering firms are developing several options based on both ECF and TCF bleaching systems. For example, Eka Nobel, a supplier of chlorine dioxide, and Jaakko Pöyry, an engineering consulting firm, are currently testing their ECF effluent-free technologies at a mill in Finland. Mills that operate effluent-free *bleach plants* may not operate effluent-free *mills*. Spills, leaks and wastewater purges throughout the mill have to be managed. In some cases, this effluent will be treated and released.

- In the TCF process, mills would recirculate all bleach plant filtrate to the chemical recovery system. Process water would be recovered from the evaporators and the organic waste and the used bleaching chemicals would go to the recovery boiler, where the bleaching chemicals would be recovered and the organic waste would be burned. By replacing its final chlorine dioxide stage with hydrogen peroxide, Union Camp could move to an effluent-free TCF bleach plant.

- Researchers are exploring several different strategies to "close up" ECF bleach plants. Zerotech, a joint venture of Millar Western and NLK, proposes an independent system that would evaporate and incinerate all the filtrate from the bleach plant.[15] Eka Nobel and Jaakko Pöyry are evaluating a similar process.[16]

- Other ECF options would handle the alkaline and acid bleach plant filtrates separately. The untreated alkaline effluent would be sent to the chemical recovery system. The acid filtrate would either be treated and reused within the mill, or evaporated with disposal of the concentrated residues.[17]

- With some manufacturing process modifications to reduce the concentration of chloride ions in the effluent, Champion's BFR™ process might be extended to include the final chlorine dioxide bleaching stage. The mill demonstration of BFR™ will include the final bleaching stage.[18]

As mills reduce the amount of bleach plant filtrates they have to manage a range of metals and other non-process elements that may build up over time. Both ECF and TCF effluent-free systems must overcome these technical challenges. Wood contains small quantities of metals and chlorides that are traditionally discharged in very low concentrations in mill effluent.

- Calcium and other metals can precipitate out of the alkaline bleach plant filtrates to cause scaling on pipes.[19]

- Increased levels of potassium may require adjustments to recovery boiler operations because it changes the properties of the molten smelt.[20]

- Both ECF and TCF effluent-free processes will have to manage increased chloride levels, although chloride levels in the bleach plant filtrates from TCF processes will be lower than that from ECF processes. Filtrates with high chloride levels may cause corrosion in the recovery boiler. Incinerating organic and inorganic chlorides may increase air emissions of dioxins and their concentration in the ash.[21]

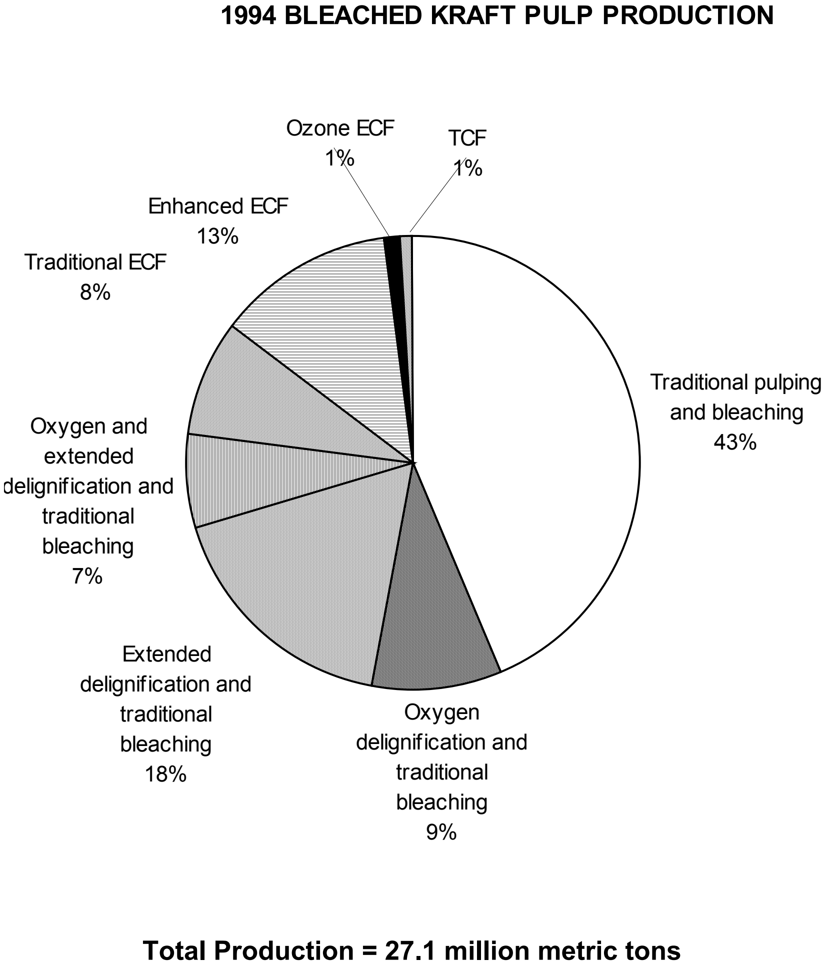
- Mills with TCF processes must control the concentrations of manganese and iron to prevent the degradation of ozone and hydrogen peroxide. Mills use chelating agents to dissolve the metals and then wash the pulp to remove them. Recirculating the filtrate from the chelating stage poses some challenges because of its metal content and acidity. Louisiana-Pacific plans to send some of these filtrates to the chemical recovery system, where the metals will be removed as solid waste.[22]

5. Current Status of Bleached Kraft Mill Manufacturing Technologies

a) Base Case Processes

Eighty-seven bleached kraft mills currently operate in the U.S. 84 of these mills produce papergrade kraft pulp exclusively, while 3 mills produce dissolving pulp as well.[23] These mills used a combination of pulping and bleaching technologies to produce 27.1 million metric tons of pulp in 1994. **Figure 1** illustrates the range of manufacturing technologies used by U.S. mills in 1994. U.S. mills used some elemental chlorine to produce 20.8 million metric tons of pulp. Initially, mills substituted a small amount of chlorine dioxide for the chlorine in the first bleaching stage to improve pulp strength, but in response to the discovery of dioxins in bleached kraft mill effluent in 1985, many mills have increased the chlorine dioxide substitution levels from 10-50% to 70-100%. Mills also are eliminating sodium hypochlorite from the bleach plant as a control strategy for chloroform, which EPA has identified as a hazardous air pollutant. Chloroform is a probable human carcinogen.[24]

Figure 1. Estimates of U.S. bleached kraft pulp production in 1994



Notes: We based the estimates of annual production on 350 days of operation per year and a 95% operating rate.

Sources:
[1] U.S. EPA (Office of Pollution Prevention and Toxics), *Pollution Prevention Technologies for the Bleached Kraft Segment of the U.S. Pulp and Paper Industry* (Washington, DC: EPA/600/R-93/110, 1993), 4-18-21, 4-41.
[2] Paul Wiegand, NCASI, letter to Ron Jordan, Office of Water, U.S. EPA, March 3, 1995
[3] Kelly H. Ferguson, "Union Camp Begins Ozone Era with New Kraft Bleaching Line at Franklin, VA," *Pulp & Paper*, **66(11)**: 42 (1992).
[4] Anton Jaegel and Kirk Girard, "TCF Bleaching at Louisiana-Pacific Corp.'s Samoa Pulp Mill, Calif.," *Proceedings of the 1995 International Non-Chlorine Bleaching Conference* (San Francisco: Miller Freeman Inc., March 1995).
[5] *Trends in World Bleached Chemical Pulp Production: 1990-1995*, (Washington, DC: Alliance for Environmental Technology, April 1995), 4.

b) Traditional And Enhanced ECF Processes

In 1994, 8 U.S. mills produced approximately 2.3 million metric tons of pulp using traditional ECF manufacturing processes, while 10 U.S. mills produced approximately 3.5 million metric tons of bleached kraft pulp using enhanced ECF processes. In 1994, of the 72 million metric tons of bleached chemical pulp produced worldwide, ECF pulps accounted for 23.5 million metric tons of this total.[25] In 1995, volumes of ECF pulp are projected to be 28.0 million metric tons.[26]

6. Low-effluent ECF and TCF processes

Ozone bleaching is a new technology that a number of U.S. mills are evaluating. Union Camp has been operating a 900 ton per day ozone **ECF** bleach line at its Franklin, VA mill with about 80% filtrate recycling since the fall of 1992.[27] Since Union Camp announced the start-up of its bleached southern pine line that includes an ozone bleaching stage, six ozone bleaching stages have been installed in bleached kraft mills worldwide and four more will be installed by 1996.[28] Consolidated Papers Inc. plans to install high consistency ozone bleaching at its Wisconsin Rapids, WI kraft mill. In June 1994, Champion announced that it was beginning an 18-month mill-scale trial of its BFR™ technology at its Canton, NC mill. Champion plans to start this demonstration in the fall of 1995.

Louisiana-Pacific's Samoa, CA softwood **TCF** kraft pulp mill, for example, currently recirculates 70% of the filtrate from its TCF bleach plant through oxygen and brownstock washers to the recovery boiler.[29] Lövblad of Södra Cell reports that its Värö, Sweden mill recirculates 75% of the filtrate from the bleach plant.[30] Several Swedish mills have installed ozone bleaching stages to make TCF pulp and to move toward the effluent-free bleach plant. Since January 1995, MoDo has operated the ozone TCF hardwood bleach line at its kraft mill in Husum, Sweden in an effluent-free mode one or two weeks at a time.[31]

At the 1995 International Non-Chlorine Bleaching Conference, producers of TCF pulp from companies around the world reported on the quality of their TCF pulps. Mills have been able to produce commercial quantities of full brightness TCF softwood pulps with a 5% decrease in tear strength as compared to a full brightness ECF pulp. All other properties were similar. 85 GE brightness TCF pulps have similar strength and optical properties to ECF pulps.[32]

II. FINDINGS

The findings have been divided into four sections: energy consumption, air emissions, effluent, and solid waste generation associated with the production of the base case, traditional ECF, enhanced ECF and low-effluent ECF and TCF bleached kraft pulp. The data on which these findings are based show significant variability because of the range of ages and geographical locations of the mills, as well as differences in the processes that mills use to produce a given type of pulp. In some cases, few data exist because mills do not have extensive operating experience with these technologies.

We describe some general trends and present findings for specific parameters in this section. The specific findings compare the magnitude of energy and environmental releases generated by the bleached kraft pulp manufacturing processes. On average, reducing the magnitude of energy consumption and environmental releases reduces the potential environmental impacts associated with bleached kraft pulp production; however, because most of the releases considered in this paper have local environmental effects, *their impact on the environment will vary with the receiving environments of individual mills.* The section of the paper that contains the supporting research for each finding is indicated in bold type at the end of each finding.

A. Energy consumption of Bleached Kraft Pulp Manufacturing Processes

We compare the energy required to produce a metric ton of bleached kraft pulp using traditional ECF, enhanced ECF and low-effluent ECF and TCF bleaching sequences. These estimates include the energy required to manufacture the chemicals off-site. **[Sections III. B, III. C]**

General trends and observations:

As oxygen-based bleaching agents replace chlorine dioxide, the energy required to produce bleached kraft pulp decreases. Although producing a metric ton of ozone requires about 12% more energy than does the production of a metric ton of chlorine dioxide, 1 kg ozone replaces about 2 kg of chlorine dioxide, so the bleach plant energy consumption of ozone ECF sequences is lower than that of traditional ECF processes. The increased energy savings that results from recirculating the bleach plant filtrates to the chemical recovery system reduces the purchased energy requirements of low-effluent processes as compared to the enhanced ECF processes.

Specific findings:

- **Enhanced ECF bleaching processes consume less total and purchased energy than either the base case or traditional ECF processes. when energy savings are considered.** The total energy consumed by the enhanced ECF processes is about 20% and 34% lower, respectively, than that of the base case or traditional ECF processes. The purchased energy consumed by enhanced ECF pulp consumes is about 34% and 47%, respectively, than that of the base case and traditional ECF bleaching sequences.

- **The total energy consumption of an enhanced ECFprocess, low-effluent ozone ECF process, a low-effluent ozone TCF process and an enhanced ECF process with BFR™ vary by 9%.**

- **The low-effluent ozone ECF and TCF processes have the lowest purchased energy requirements of the pulp manufacturing processes studied.**

B. Air Emissions from Bleached Kraft Mill Sources

We have examined the magnitude of the emissions of hazardous air pollutants (HAPs), volatile organic compounds (VOCs) and total reduced sulfur compounds (TRS) from the process sources at bleached kraft mills. These air emissions affect the local environment around the mill. This analysis considers mills with the base case, traditional and enhanced ECF bleaching sequences. Insufficient data precluded the comparison of air emissions from mills with low-effluent and effluent-free bleaching processes.

General trends and observations:

Chloroform emissions decrease as the quantity of chlorine and chlorine dioxide used decreases. HAP and VOC emissions may increase as mills reuse more process water.

Specific Findings:

Hazardous air pollutants (HAPs) [Section IV. B]:

- **Methanol accounts for most of the HAP emissions from the pulp mill and bleach plant sources.**

- **Chloroform emissions decrease with the elimination of elemental chlorine and may decrease with lower chlorine dioxide charges in the first bleaching stage.** The NCASI 16 mill study indicates that the bleach plant chloroform emissions are lowest for the mill with enhanced ECF bleaching; however, more sampling is required to determine whether the chloroform emissions from a mill with oxygen delignification are *statistically* lower than those from mills with traditional ECF processes.

- **Process water reuse increases the emissions of HAPs from oxygen delignification systems.** These emissions may decrease as mills either steam-strip the condensates from the black liquor evaporators or use filtrate from the bleach plant in the post-oxygen washers.

- **Mills that move toward ECF effluent-free bleach plants may generate dioxin emissions from either the recovery boiler or the dedicated incinerator if organic compounds are burned in the presence of chlorides. The dioxins generated in combustion processes have six to eight chlorines, and are up to one thousand times less toxic than dioxins with four chlorines.**

Volatile organic compounds (VOCs) [Section IV. C]:

- **The differences in VOC emissions among the bleached kraft pulping processes studied is small.** The VOC emissions from bleached kraft mills with traditional ECF bleaching are about 7% lower than those of the base case mill, while VOC emissions from an enhanced ECF mill with oxygen delignification range from 4% lower than the base case mill to about 10% higher depending on the source of the water used in the oxygen delignification system.
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Total reduced sulfur compounds (TRS) [Section IV. D]

- **Generally, installing the technology options considered in this paper has little effect on the TRS emissions from bleached kraft mills, although installing extended delignification may lower these emissions.** The pulping and chemical recovery systems are the major sources of TRS at bleached kraft mills.

C. Effluent from Bleached Kraft Mills

In this section, we examined the effect of traditional ECF, enhanced ECF and low-effluent ECF and TCF bleaching processes on the magnitude of the loading of BOD, COD, color, AOX and dioxins in bleach plant filtrates or treated mill effluent. Effluent discharge affects mills' receiving water. Some effects are localized to the area close to the point of discharge, while the organic material that degrades slowly may be transported long distances. Currently, the environmental impacts of BOD are controlled by national effluent limitations and by local permitting and monitoring as well. Some states control color and COD releases as well.

We also examined several studies that examine the environmental effects of effluent from ECF and TCF bleached kraft mills, along with research that has suggested that there are unidentified substances of concern in bleached kraft mill effluent.

General trends and observations:

Replacing elemental chlorine with chlorine dioxide reduces the loading of AOX and dioxins in treated mill effluent, but has little effect on BOD COD or color. Reducing the amount of lignin in the pulp before it enters the bleach plant and reducing bleach plant effluent flow result in large decreases in all summary parameters. The following practices reduce the amount of organic material in bleached kraft pulp mill effluent and, as a result, the potential impacts of treated bleached kraft mill effluent on the aquatic ecosystems: (1) installing spill reclamation systems; (2) upgrading brownstock washing; (3) installing extended delignification and oxygen delignification to remove lignin before the pulp enters the bleach plant; and (4) modifying the bleaching sequence to recirculate the bleach plant filtrate.

Specific findings:

Effluent Quality:

BOD, COD and color [Sections V. B.1 and V. B.2]:

- **Moving to traditional ECF bleaching from 50% chlorine dioxide substitution has no observable effect on the magnitude of these effluent parameters.**

- **Using extended delignification and/or oxygen delignification to reduce the amount of lignin in the pulp before it enters the bleach plant reduces the loading of BOD, COD, and color in bleach plant filtrates.**

- **Installing low-effluent ECF or TCF processes decreases the loadings of all three effluent parameters to the lowest level of the options considered.**

AOX [Section V. B.3]:

In the regulatory impact assessment of the proposed effluent guidelines, EPA states some of the issues associated with controlling AOX. “Although AOX concentrations can be used to determine the removal of chlorinated organics to assess loading reductions, they do not provide information on the potential toxicity of the effluent, and therefore, are not appropriate to evaluate the potential impacts on the environment. Although no statistical relationship has been established between the level of AOX and specific chlorinated organic compounds, AOX analysis can be an inexpensive method for obtaining the "bulk" measure of the total mass of chlorinated organic compounds.”[33] Although current studies have not found a link between AOX and environmental effects, AOX is a good measure of the amount of elemental chlorine in the bleaching process.

- **The mean AOX loading in the softwood bleach plant filtrates with traditional ECF bleaching is about 25% lower than that of the base case.** Increasing the chlorine dioxide substitution in the first bleaching stage reduces the mean AOX loading in the bleach plant filtrates to 1.5 kg/air-dried metric ton (ADMT) of pulp from a loading of about 2.0 kg/ADMT in the bleach plant filtrates of the base case mill.

- **The mean AOX loading in treated softwood bleached kraft mill effluent of a mill with enhanced ECF bleaching is about 63% lower than the mean loading in the bleach plant filtrates of the base case.**

- **Recirculating the bleach plant filtrates from the alkali extraction stage to produce low-effluent ECF pulps reduces the AOX loading in the bleach plant filtrates to the lowest level of the ECF options considered.**

- **The AOX loading of TCF bleach plant filtrates is at background levels and is the lowest of the manufacturing technologies considered.**

Dioxins [Section V. B.4]:

- **Increasing the chlorine dioxide substitution from 50%-100% in the first bleaching stage reduces the concentrations of both TCDD and TCDF in treated bleached kraft mill effluent below the analytical detection limit of 10 ppq.**

- **The variability of the data precludes determining the effect of installing oxygen delignification or extended delignification on the dioxin loading in the treated final effluent of bleached kraft mills with ECF bleaching sequences.** Data show that the mean loading of TCDF in final effluent from enhanced ECF mills is lower than that from traditional ECF mills; however, statistical analysis indicates that these means are not statistically different. Current analytical methods are not sensitive enough to measure these dioxin loadings precisely. Additional research is required to determine whether installing oxygen delignification or extended delignification lowers the TCDF loading in the final effluent.

- **Mills that replace chlorine dioxide with ozone in the first bleaching stage may not generate dioxins.**

Effluent toxicity studies - Bleach plant filtrates [Section V. C.1]:

- **A Canadian laboratory study showed that filtrates from both traditional and enhanced ECF bleaching processes were less toxic to water flea reproduction and fathead minnow growth than were filtrates with 50% chlorine dioxide and 50% elemental chlorine.**

- **This study also showed that bleach plant filtrates from an enhanced ECF bleaching process had fewer chronic toxic effects to water fleas and fathead minnows than did filtrates with traditional ECF bleaching.**

- **Two studies of laboratory-prepared filtrates from enhanced ECF and TCF processes indicated that the untreated TCF filtrates were more toxic to several freshwater and marine organisms than were untreated ECF filtrates. The differences in the sublethal toxicity of treated ECF and TCF filtrates is small.** Excess hydrogen peroxide or sodium meta-bisulfite used to neutralize the peroxide may account for the toxicity of the TCF filtrates.

- **A large, highly colored, water soluble, degraded lignin molecule found in bleach plant effluent is toxic to the early life stages of marine plants, invertebrates and fish.**

Effluent toxicity studies - Mill studies [Section V. C.2]:

- **The results from current studies comparing ECF and TCF bleach plant filtrates from mills that bleach pulp with similar lignin content show little difference in chronic toxicity.** While a range of single species bioassays show that treated TCF mill effluents are less toxic than treated ECF mill effluents, model ecosystem studies do not show significant differences in the effluent from mills with similar pulping technologies.

- **Recent research suggests that exposure to compounds in the black liquor may reduce the reproductive capacity of wild fish downstream from bleached kraft mills. Laboratory research suggests that plant sterols may account for these effects.**

D. Solid Waste Generation at Bleached Kraft Mills

In this section we discuss the quantity and quality of the solid waste generated by mills that use the three technology options.

General trends and observations:

Solid waste generation becomes a greater technical issue as mills approach effluent-free bleach plant operation, because the metals, nutrients and other non-process elements that used to leave with the effluent may need to be handled as solid waste. All effluent-free bleaching processes must manage these residues. Mills with ECF effluent-free processes may have to handle ash from the separate incineration of evaporator residues, as well.

- **Installing traditional ECF, enhanced ECF or low-effluent ECF bleaching processes reduces the loading of chlorinated organic compounds and dioxins in wastewater sludge. The concentrations of these compounds in sludge from TCF mills should be at background levels because these mills do not use chlorine compounds.**

- **Engineers predict that for mills with effluent-free bleach plants that recirculate the bleach plant filtrate to the chemical recovery system, the quantity of solid waste generated may increase. Additional research is needed to determine whether some of these wastes will be hazardous or difficult to dispose of.**

- **Mills that send filtrate from ECF bleach plants to a separate recovery system may have to dispose of ash if the mill incinerates the organic waste. Additional research is needed to determine whether the resulting ash contains dioxins, and thus needs to be handled as hazardous waste.**

III. ENERGY CONSUMPTION OF BLEACHED KRAFT PULP MANUFACTURING TECHNOLOGIES

A. Scope and Sources

In this paper, we compare estimates of the energy required to bleach kraft pulp using the processes of interest. This analysis considers the total energy required to produce the bleaching chemicals and mix them with the pulp, and the purchased energy which accounts for the energy savings that result as the filtrate from bleaching stages is recirculated to the chemical recovery system. Mills with low-effluent bleaching processes produce additional steam from the recovery system and reduce the energy required to obtain fresh water and to treat the effluent. Readers interested in the energy consumed to produce a ton of bleached kraft pulp from wood chips should see Section III of White Paper No. 10A.

The task force has evaluated several published studies as well as information presented at technical meetings. These studies estimate the energy consumed in the bleaching process to produce a metric ton of bleached kraft pulp. The magnitude of the estimates depends on several factors: the amount of lignin removed before the first bleaching stage, the amount of each chemical used and the energy required to produce the chemical itself.

B. Power Required to Manufacture Bleaching Chemicals

We present the energy required to produce the various bleaching chemicals in **Table 2**. **Table B-1** in Appendix B contains the detailed calculations of these data. Chlorine dioxide and ozone consume the most energy in their manufacture, but the bulk of the power to produce chlorine dioxide is consumed off-site by the plants that produce sodium chlorate. Increasing the use of oxygen and ozone increases the electricity demand at the mill, but lowers the total energy demand. Oxygen requires relatively little energy to produce on site. The fact that one kilogram of ozone can replace from 1.5 to 2.0 kilograms of chlorine dioxide further lowers the power requirements associated with ozone bleaching processes.[34]

Table 2. Energy required to produce bleaching chemicals

Bleaching Chemical	**Energy consumption** (millions of Btu's/ metric ton)
Ozone	131.4
Sodium hydroxide	14.7
Chlorine	14.7
Chlorine dioxide	117.6
Hydrogen peroxide	34.8
Oxygen (1)	4.2
Oxidized white liquor (2)	41.1
Sulfuric acid	1.1

(1) Mills that use ozone do not require additional power to produce oxygen
(2) Mills generally use oxidized white liquor as the source of sodium hydroxide in oxygen delignification systems.

C. Energy Consumption of the Technology Options

We present estimates of the total and purchased energy consumed by the bleaching processes in **Figure 1**. The estimates of total energy include the energy required to produce the bleaching chemicals and the electricity and steam consumed to operate the bleach plant. **Table B-2** in Appendix B provides the calculations of the energy required to manufacture the bleaching chemicals. Union Camp provided estimates of the quantities of chemicals used in the bleaching sequence to produce 90 GE brightness softwood bleached kraft pulp, along with estimates of the electricity and steam consumed in the bleach plant.[35] **Table 3** presents the calculation of total and purchased energy for the different processes.

Replacing the elemental chlorine in the base case with chlorine dioxide in a traditional ECF process increases the energy requirement by 20%, while installing an enhanced ECF process with oxygen delignification reduces the energy requirement by 20%. Installing oxygen delignification or extended delignification reduces the energy required to produce ECF pulp by reducing the amount of chlorine dioxide in the bleaching sequence. case. The total energy consumption of low-effluent high consistency ozone ECF and TCF processes is about the same as that of the enhanced ECF processes. The total energy consumption projected for an enhanced ECF process with BFR™ is slightly higher than that of an enhanced ECF process because of additional evaporator requirements.[36] A comparison of the energy consumption of the low-effluent ozone ECF and TCF processes demonstrates that the power requirements decrease as oxygen, ozone and hydrogen peroxide replace chlorine dioxide in the bleaching process.

Table 3. Estimates of energy usage and savings for different pulping processes for 90 GE brightness softwood pulp (millions of Btu's/air-dried metric ton of pulp)

Bleaching process	$C_{50}D_{50}$EDED	D(EO)DED	OD(EO)D	OZ(EO)DD	OZQPZP	OD(EO)D + BFR™
Energy to manufacture chemicals (1)	7.59	10.19	5.03	4.99	3.58	5.43
Direct equipment power (2)	0.92	0.92	1.32	1.51	2.21	1.32
Process steam (3)	4.39	4.39	3.80	3.09	3.80	3.80
Recovery steam credit (4)	0.00	0.00	-1.62	-2.66	-2.66	-2.66
Water supply credit (5)	0.00	0.00	-0.26	-0.29	-0.29	-0.29
Effluent treatment credit (6)	0.00	0.00	-0.13	-0.15	-0.15	-0.15
TOTAL ENERGY	**12.9**	**15.5**	**10.2**	**9.6**	**9.6**	**10.5**
Energy savings	**0.0**	**0.0**	**2.0**	**3.1**	**3.1**	**3.1**
PURCHASED ENERGY	**12.9**	**15.5**	**8.2**	**6.5**	**6.5**	**7.4**

Note: The energy data include the transmission losses associated with generating electricity at a utility; thus 1 kilowatt hour of electricity equals 10,500 Btu's of energy.

(1) Energy required to make the bleaching chemical.
(2) Running power consumed by the bleach plant equipment
(3) Process steam energy required (converted into kWh/metric ton)
(4) Credit for recovery boiler steam used (assuming that O stage solids are recovered for O(CD)ED and ODED cases, and O, Z and E stage solids are recovered for the OZQPZP case)
(5) Water supply energy credit based on reduced deep well pumping
(6) Effluent treatment energy credit based on reduced BOD treatment requirements in an aerated lagoon.

Most researchers report lower energy consumption for TCF bleaching sequences. Laxén and Henricson estimated a 50% decrease in the energy consumed by a mill with a four stage bleaching process when it replaced a low kappa ECF bleaching sequence with an ozone-based TCF sequence.[37] Other researchers reported that reducing the Kappa number of an oxygen delignified pulp from 18 to 8 with extended delignification reduced the power requirement for an ECF bleaching sequence from 260 to 150 kWh/ADMT, a 42% reduction. Moving to an ozone TCF bleaching sequence reduced the power consumption to 96 kWh/ADMT.[38] Lövblad found a 35% decrease in the bleaching chemical manufacturing power requirement and a 10% decrease in the total mill power required to produce 80 ISO brightness softwood pulp when Södra Cell's Värö, Sweden mill switched from an enhanced ECF bleaching sequence with extended delignification and oxygen delignification to a peroxide-based TCF sequence.[39]

The purchased energy estimates include Union Camp's estimates of energy savings that result from (1) recovery boiler steam used, (2) reduced energy to pump water from deep wells, and (3) reduced effluent treatment energy because of the lower effluent flow.[40] The low-effluent ozone ECF and TCF processes have the lowest purchased energy requirements of the pulp manufacturing processes studied. These processes have the total energy requirement and the largest energy savings. The projected energy consumption for an enhanced ECF process with BFR™ is slightly higher.

Neither Union Camp[41] nor Champion International[42] expect to see the significantly higher energy consumption for the effluent-free bleach plants for systems that recirculate the bleach plant filtrates to the chemical recovery system. Separate bleach plant filtrate evaporation systems as proposed by Eka Nobel, may increase energy consumption as a result of the increased load on the evaporators..[43]

D. Summary

- **Enhanced ECF bleaching processes consume less total and purchased energy than either the base case or traditional ECF processes. when energy savings are considered.** The total energy consumed by the enhanced ECF processes is about 20% and 34% lower, respectively, than that of the base case or traditional ECF processes. The purchased energy consumed by enhanced ECF pulp consumes is about 34% and 47%, respectively, than that of the base case and traditional ECF bleaching sequences.

- **The total energy consumption of an enhanced ECF process, low-effluent ozone ECF process, a low-effluent ozone TCF process and an enhanced ECF process with BFR™ vary by 9%.**

- **The low-effluent ozone ECF and TCF processes, have the lowest purchased energy requirements of the pulp manufacturing processes studied.**

IV. AIR EMISSIONS FROM BLEACHED KRAFT MILL PROCESS SOURCES

A. Scope and Sources

In this section, we examine estimates of hazardous air pollutants (HAPs), volatile organic compounds (VOCs) and total reduced sulfur compounds (TRS) from process sources at bleached kraft mills with the base case, traditional ECF, enhanced ECF and low-effluent TCF processes. These sources include the pulp and bleach plants and the chemical recovery system. White Paper NO. 10A presents a discussion of the energy-related air emissions including sulfur dioxide, nitrogen oxides, particulates and carbon dioxide emissions associated with the production of paper with a bleached kraft pulp furnish.

We have used emission data from the 1994 NCASI study of the release of 28 organic HAPs, VOCs and TRS compounds from 16 mills – nine bleached kraft mills, four unbleached kraft mills, two sulfite mills and one unbleached semichemical pulp mill.[44] NCASI recently performed a similar analysis at Louisiana-Pacific's low-effluent TCF softwood bleached kraft pulp mill in Samoa, CA.[45] In Appendix B, we present a summary of the emissions of ten HAPs from sources at bleached kraft mills in **Table B-5**, and VOCs and TRS emissions in **Table B-6**.

We do not have information on the HAP, VOC or TRS emissions from low-effluent ECF bleached kraft mills. Champion will perform air emission testing as part of its demonstration of the BFR™ technology.[46] No air emission data currently exists for mills with effluent-free bleach plants because none are in operation today.

B. Hazardous Air Pollutants (HAPs)

The EPA has defined HAPs as any of the 189 substances listed in section 112(b) of the 1990 Clean Air Act Amendments.[47] We included compounds from the NCASI study that comprised a minimum of one percent of the total HAPs from any source from the mill. We present the HAP emissions from all sources at the mill in **Table B-3** of Appendix B.

Studies have shown that acetaldehyde, formaldehyde and chloroform, three HAPs emitted by bleached kraft mills, can cause cancer in animal livers and degeneration of animal olfactory epithelium. Other compounds can exhibit toxic effects above a threshold level.[48] HAP emissions affect the local environment around the mill. These emissions are regulated to maintain releases at the mill fence line below levels that cause these toxic effects in the laboratory. Mills control these releases with chemical scrubbers and by routing the releases from vents to the lime kiln or another power boiler where these compounds are burned as fuel.

Major bleached kraft mill non-combustion sources include the pulp and bleach plants, storage tanks and the chemical recovery system which includes the recovery boiler. We have used the average emissions from the 12 brownstock washing systems,[49] six oxygen delignification systems[50] and ten recovery boilers that NCASI tested.[51] Methanol, chloroform, acetaldehyde, methyl ethyl ketone and formaldehyde account for most of the HAPs emitted by a bleached kraft mill. We present the major HAP emissions from the process sources at the mill and from the bleach plant in **Table 4.**

Table 4. HAP emissions from bleached kraft mill sources

Base case (50% D substitution)			
HAP	**Pulp mill sources** (lb/ODTP)	**Bleach Plant sources** (lb/ODTP)	**Bleach plant sources/ pulp mill sources**
Total	**2.54**	**0.68**	**26.7%**
Methanol	2.18	0.52	23.8%
Acetaldehyde	0.08	0.00	0.0%
Formaldehyde	0.02	0.00	0.0%
Chloroform	0.13	0.12	92.3%
Traditional ECF bleached kraft mill			
HAP	**Pulp mill sources** (lb/ODTP)	**Bleach Plant sources** (lb/ODTP)	**Bleach plant sources/ pulp mill sources**
Total	**2.132**	**0.270**	**12.7%**
Methanol	1.912	0.250	13.1%
Acetaldehyde	0.085	0.003	3.5%
Formaldehyde	0.019	0.000	0.0%
Chloroform	0.021	0.011	52.4%
Enhanced ECF bleached kraft mill			
HAP	**Pulp mill sources** (lb/ODTP)	**Bleach Plant sources [1, 2]** (lb/ODTP)	**Bleach plant sources/ pulp mill sources**
Total	**3.193 (2.402)**	**1.329 (0.54)**	**41.6% (22.5%)**
Methanol	2.932 (2.182)	1.270 (0.52)	43.3% (23.8%)
Acetaldehyde	0.128 (0.094)	0.047 (0.012)	36.7% (12.7%)
Formaldehyde	0.021 (0.020)	0.002 (0.000)	9.5% (0.0%)
Chloroform	0.013 (0.014)	0.002 (0.002)	15.4% (14.3%)
Low-effluent TCF kraft mill			
HAP	**Pulp mill sources** (lb/ODTP)	**Bleach Plant sources [1, 2]** (lb/ODTP)	**Bleach plant sources/ pulp mill sources**
Total	**2.596**	**0.158**	**6.1%**
Methanol	2.338	0.135	5.8%
Acetaldehyde	0.111	0.029	26.1%
Formaldehyde	0.041	0.021	52.2%
Chloroform	0.000	0.000	0.0%

[1] Bleach plant sources include the oxygen delignification system and the bleach plant.

[2] Numbers in parentheses include emissions from an oxygen delignification system that used fresh shower water (Mill N).

The chloroform emissions of the three mills in **Table 4**, indicate that these emissions decrease by about 90% in mills that substitute chlorine dioxide for all of the elemental chlorine in the first bleaching stage. Bleach plant air emissions of chloroform decreased from 0.12 lb/ODTP for the bleach plant with 50% chlorine dioxide substitution to 0.002 lb/ODTP for the bleach plant at a mill with an enhanced ECF process.[52] Chloroform emissions from the mill with the low-effluent TCF process are below the limit of detection. This measured reduction in chloroform emissions supports the hypothesis that once a mill has eliminated hypochlorite from the bleaching process, the formation of chloroform depends on the amount of elemental chlorine present in the first bleaching stage. According to an earlier NCASI study, mills with 100% chlorine dioxide substitution may emit less than 0.02 pounds of chloroform to air and water per ton of pulp.[53]

The control of HAP emissions from oxygen delignification stages may be a particular need for mills with enhanced ECF bleaching sequences. Of the bleached kraft pulping processes, the bleached kraft pulp mill with oxygen delignification had the highest total HAP emissions of the bleached kraft pulp mills, because some methanol, methyl ethyl ketone, acetaldehyde and formaldehyde are emitted from the oxygen delignification system. NCASI has shown that the source of the water used on the post-oxygen showers determines the quantity of HAPs released from this source. Studies to determine whether oxygen delignification systems generate methanol were inconclusive.[54] Mills tend to reuse process water in the oxygen stage as part of their water conservation programs.

For mills that use chlorine dioxide in the first bleaching stage, the clean condensates from the black liquor evaporators are often used because the chloride levels of the bleach plant filtrates are too high to recirculate to the recovery boiler. During oxygen delignification, some of the HAPs and VOCs in the condensates are released into the environment. Treating the condensates in the secondary treatment system may also result in HAP and VOC emissions because volatile compounds can be stripped from the effluent during treatment. The NCASI study did not measure fugitive emissions from mill or secondary treatment system sources.

Mills that use ozone in the first bleaching stage and TCF mills can use the bleach plant filtrates in the post-oxygen washers. The emissions data for the low-effluent TCF mill in **Table 4** indicate that reusing bleach plant filtrates generally results in lower HAP emissions than does using condensates. Mills can also use steam-stripping to remove the HAPs from the condensates and burn them as fuel in the lime kiln. Weyerhaeuser Canada reported removal of 95% of the methanol from the condensates at its Grande Prairie, Alberta mill.[55]

Recent research has confirmed that dioxins can be formed in the high temperature zones that follow combustion when sources of carbon, oxygen and chlorine are present.[56] Burning chlorinated organic compounds can also generate dioxins.[57] Dioxins generated by combustion processes generally have six to eight chlorines and are up to 1000 times less toxic that TCDD, as a result.**[58]** Thus, mills that move to effluent-free systems with ECF bleach plants may generate dioxins as chlorinated organic compounds and inorganic chloride salts are burned in the recovery boiler or in a dedicated incinerator. Mills that recover the pulp and bleach plant filtrates jointly as does Champion's experimental BFR™ process, may find increased emissions from the recovery boiler. EPA described recovery boilers (mean annual release of 2.7 g TEQ for all recovery boilers) as a relatively minor combustion source of dioxins on a national scale, but noted that local impacts may be important to evaluate.[59] Mills that recover the bleach plant filtrate separately as do processes being developed by Zerotech and Jaakko Pöyry, may find increased dioxin emissions from the incinerators. Developers of effluent-free ECF processes plan to monitor potential air emissions of dioxins as part of their feasibility studies. In addition, other HAP emissions may increase slightly as more process water is reused.[60]

C. Volatile Organic Compounds (VOCs)

Volatile organic compounds are defined as "any organic compound which participates in atmospheric photochemical reactions,"[61] and include a broad class of organic gases such as vapors from solvents and gasoline. Trees and other plants also produce VOCs, with especially high emissions in hot weather. The control of VOC emissions is important because these compounds react with nitrogen oxides (NO_x) to form ozone in the atmosphere, the major component of photochemical smog.[62] VOC emissions impact the local environment around the mill. We consider VOCs separately from HAPs because not all VOCs are classified as be HAPs. Before EPA determined that acetone was not sensitive to sunlight,[63] it was, considered to be a VOC; it is not a HAP.

Note of Caution: We cannot directly compare the total HAP and total VOC emissions from a given source. NCASI used a different method to measure the total HAP and VOC emissions. VOC emissions are measured as pounds of carbon per oven-dried ton of pulp (lb C/ODTP).[64]

We present total VOC emissions for mills with the base case, traditional and enhanced ECF bleaching sequences in **Table 5**. Because NCASI did not measure VOC emissions from the mill with 100% D substitution,[65] we used similar VOC emissions from the bleach plant of the mill with the enhanced ECF process. While the contribution to VOC emissions from the bleach plant ranges from 1%-23% respectively for traditional ECF and enhanced ECF bleaching sequences, the VOC emissions from the traditional ECF kraft mill are about 12% *lower* than the VOC emissions from the base case mill. As with HAPs, the VOC emissions from enhanced ECF processes with oxygen delignification depend on the water used in the oxygen delignification process. The VOC emissions range from *6% lower* than the base case mill emissions when the mill uses fresh water to about 20% *higher* than those of the base case mill when the mill uses condensates.

Table 5. VOC emissions from bleached kraft mill sources

Base case (50% D substitution)		**Traditional ECF bleached kraft mill**	
Source	**Quantity** lb C/ODTP	**Source**	**Quantity** lb C/ODTP
Pulping	1.11	Pulping	1.11
Bleaching	0.31	Bleaching	0.03
Chemical Recovery	0.97	Chemical Recovery	0.97
Total	**2.39**	**Total**	**2.11**

Enhanced ECF bleached kraft mill with OD	
Source	**Quantity** lb C/ODTP
Pulping	1.11
Bleaching [1, 2]	0.68 (0.15)
Chemical Recovery	0.96
Total	**2.92 (2.24)**

[1] Bleaching sources include the oxygen delignification system and the bleach plant.

[2] Numbers in parentheses include emissions from an oxygen delignification system that used fresh shower water (Mill N).

D. Total Reduced Sulfur Compounds (TRS)

Total reduced sulfur compounds include hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide. The NCASI study did not measure hydrogen sulfide emissions at any of the mills. While these compounds are not considered to show acute toxicity, systematic surveys of odor pollution caused by pulp mills have supported the link between odor and respiratory responses.[66] TRS emissions affect the local environment around the mill.

The pulping process and the chemical recovery system are the sources of TRS at a bleached kraft mill; the choice of bleaching sequence will have little effect on the emissions of these compounds. Bleached kraft mills have reduced the quantity of totally reduced sulfur compounds released by installing low-odor recovery boilers and systems that capture and incinerate these gases. Installing extended delignification may reduce TRS emissions by reducing the temperature and pressure at which the pulp leaves the digester making the TRS compounds easier to recover.[67]

E. Summary

Hazardous air pollutants (HAPs) [Section IV. B]:

- **Methanol accounts for most of the HAP emissions from the pulp mill and bleach plant sources.**

- **Chloroform emissions decrease with the elimination of elemental chlorine and may decrease with lower chlorine dioxide charges in the first bleaching stage.** The NCASI 16 mill study indicates that the bleach plant chloroform emissions are lowest for the mill with enhanced ECF bleaching; however, more sampling is required to determine whether the chloroform emissions from a mill with oxygen delignification are *statistically* lower than those from mills with traditional ECF processes.

- **Process water reuse increases the emissions of HAPs from oxygen delignification systems.** These emissions may decrease as mills either steam-strip the condensates from the black liquor evaporators or use filtrate from the bleach plant in the post-oxygen washers.

- **Mills that move toward ECF effluent-free bleach plants may generate dioxin emissions from either the recovery boiler or the dedicated incinerator if organic compounds are burned in the presence of chlorides. The dioxins generated in combustion processes have six to eight chlorines, and are up to one thousand times less toxic than dioxins with four chlorines.**

Volatile organic compounds (VOCs) [Section IV. C]:

- **The differences in VOC emissions among the bleached kraft pulping processes studied are small.** The VOC emissions from bleached kraft mills with traditional ECF bleaching are about 12% lower than those of the base case mill, while VOC emissions from an enhanced ECF mill with oxygen delignification range from 6% lower than the base case mill to about 20% higher depending on the source of the water used in the oxygen delignification system.

Total reduced sulfur compounds (TRS) [Section IV. D]

- **Generally, installing the technology options considered in this paper has little effect on the TRS emissions from bleached kraft mills, although installing extended delignification may lower these emissions.** The pulping and chemical recovery systems are the major sources of TRS at bleached kraft mills.

V. EFFLUENT FROM BLEACHED KRAFT MILLS

A. Scope

In this section we examine the impact of the manufacturing technologies on the magnitude of the releases of organic material in bleached kraft mill effluent and discuss the research on the environmental effects of this effluent on mill receiving water ecosystems.

1. Effluent quality

Bleached kraft mill effluent comes from many process sources in the mill including pulping, bleaching, chemical recovery and at integrated paper mills, the paper machines. Spills also contribute to the load of organic waste in the effluent. Bleached kraft mill effluent is a complex mixture of compounds. As of 1994, researchers have identified 415 organic substances in the bleached kraft mill effluent;[68] experts believe that the known compounds represent a fraction of the compounds in the effluent from these mills.

The organic substances dissolved or suspended in the wastewater or effluent from a bleached kraft mill are characterized by several different parameters. Biochemical oxygen demand (BOD), chemical oxygen demand (COD), adsorbable organic halogens (AOX) and color measure classes of compounds found in the effluent, and thus are called summary parameters.

Specific substances known to be toxic may also be present in the effluent. For example, trace amounts of "dioxins" are formed when elemental chlorine present during the delignification stages of the bleaching process reacts with unchlorinated dibenzo-p-dioxin and dibenzofuran precursors that are present in the wood.[69] We use the term "dioxins" herein to describe the families of chemicals known as chlorinated dibenzo-p-dioxins and dibenzofurans. These families consist of 75 different chlorinated dibenzo-p-dioxins and 135 different chlorinated dibenzofurans. These molecules can have from one to eight chlorine atoms attached to a planar skeleton of 12 carbon atoms and one or two oxygen atoms for the dibenzofurans and the dibenzo-p-dioxins, respectively. 2,3,7,8-tetrachlorodibenzo-p-dioxin **(TCDD)** and 2,3,7,8-tetrachlorodibenzofuran **(TCDF)** are two of the most toxic members of this family of compounds. If dioxins are detected in the effluent from bleached kraft mills, they are most likely to be TCDD and TCDF.[70]

Because research has shown that dioxins exert their toxic effects through one mechanism, the toxicity of different members of the dioxin and furan families are compared using toxic equivalence factors (TEF). TCDD, the most toxic compound is assigned a TEF of 1.0; scientists have found that TCDF is about one-tenth as toxic and have assigned it a TEF of 0.1. We use toxic equivalents of TCDD (TEQ) to express the toxicity of a mix of dioxins; for example, a sample that contained 1 ppq of TCDD and 1 ppq of TCDF would have 1.1 ppq TEQ of TCDD.

Dioxins are highly toxic, persistent and bioaccumulative compounds that are generated during combustion processes and chemical processes where elemental chlorine reacts with aromatic organic precursors. The toxic effects on humans and other organisms have been discussed comprehensively in several recent publications.[71] In its review of the draft dioxin reassessment, the EPA Science Advisory Board recommended that the Administrator list dioxins as a probable human carcinogen.[72] In a recent peer-reviewed article, EPA scientists reported that "available human data suggest that some individuals may respond to dioxin exposures with cancer and noncancer effects at body burdens within one to two orders of magnitude of those in the general population."[73]

EPA's current water quality criterion for the dioxin concentration in ambient water that results in an increased cancer risk in humans of one in one million (1×10^{-6}) is 0.013 parts per quadrillion (ppq). The proposed water quality criterion to protect aquatic life and wildlife is slightly lower at 0.008 ppq.[74] Depending on the quality of the effluent sample, detection limits can range from about 0.8 ppq to 10 ppq; using EPA's analytical method, the detection level at which dioxins can be quantified 99% of the time is 10 ppq. Thus, for regulatory purposes EPA has set the analytical limit of detection at 10 ppq.

2. Environmental effects

Mills have installed secondary treatment that removes resin and fatty acids and other substances that are acutely toxic to organisms in the receiving water ecosystem. Process modifications also reduce acute toxicity. Shimp and Owen reported that the undiluted, untreated effluent from an enhanced ECF mill with good spill control was not acutely toxic to zebrafish.[75] Current environmental effects research focuses on sublethal effects such as impaired growth, reproductive success or early life-stage mortality of marine organisms.

Scientists use laboratory bioassays, model ecosystems and field studies to examine the sublethal effects of the effluent on receiving water ecosystems. The laboratory bioassays examine sublethal effects or focus on sensitive life stages of organisms that represent the types of organisms found in mill's receiving waters at "environmentally relevant concentrations."[76] In model ecosystem tests, researchers expose the system to realistic concentrations of bleached kraft mill effluent in a controlled setting.[77] These studies may last from 5 to 6 months to several years. Field studies provide information about the actual effects on the organisms exposed to pulp mill effluent, but are also the most difficult to interpret. There are many other variables that affect the health of the ecosystem that cannot be controlled in field studies. Thus, researchers need to perform more controlled laboratory and model ecosystem studies to confirm effects seen in the field.

B. Bleach Plant Effluent Quality and the Manufacturing Technologies

We can compare the performance of the manufacturing technologies by examining the loading of biochemical oxygen demand (BOD), chemical oxygen demand

(COD), color, adsorbable organic halogens (AOX) and dioxins in the bleach plant filtrates.

1. Biochemical Oxygen Demand (BOD)

BOD is a measure of the tendency of an effluent to consume dissolved oxygen from receiving waters. It is also a measure of the readily biodegradable fraction of pulp mill effluent. Microorganisms in the receiving water consume oxygen as they metabolize the organic material in the effluent. High levels of BOD in the effluent stream can deprive fish, shellfish, fungi and aerobic bacteria of the oxygen they need to survive.[78] Mills employ secondary treatment systems to remove over 95% of the BOD from the raw effluent. For BOD, environmental impacts are relatively well-controlled by local permitting and monitoring. "In most cases, NPDES permits have strict limits based on the assimilative capacity of local receiving waters."[79] These limits keep BOD discharges below this level to protect aquatic communities.

a) Traditional ECF Bleaching

Increasing the percentage of chlorine dioxide substitution in the first bleaching stage results in a small decrease in the BOD loading of untreated bleach plant effluent. Secondary treatment systems, designed to remove BOD, are most effective in reducing the BOD of bleach plant effluent and effluent from other sources at the mill.

Several experts report that the level of chlorine dioxide substitution has no impact on the magnitude of the BOD loading in bleach plant filtrates when chlorine dioxide substitution in the first bleaching stage increases from 50% to 100%. Having surveyed the literature, engineers at H.A. Simons found that "there is no consistent evidence that the chlorine dioxide substitution level has any effect on the BOD of bleach plant effluent."[80] They estimate that the BOD loading in bleach plant filtrate for the base case and traditional softwood ECF mill to be 16 kg/ADMT of pulp.[81] NCASI examined the BOD loading of bleach plant filtrates from softwood kraft mills with 50% and 100% chlorine dioxide substitution in the first bleaching stages. The BOD loading in these filtrates ranged from about 11 - 16 kg/ADMT. NCASI scientists reported that the differences in BOD loading at these substitution levels were not statistically different because of the high variability of the data.[82]

b) Enhanced ECF Bleaching

Installing extended delignification and/or oxygen delignification decreases the amount of lignin that must be removed in the first bleaching stages, and the BOD loading in the untreated effluent. In **Table 6**, Renard provides the following estimates of BOD reduction in bleach plant effluent that softwood bleached kraft mills can achieve with enhanced ECF technologies.[83] The BOD loadings in the treated bleach plant effluent reflect a secondary treatment BOD removal efficiency of 92%.

Table 6. BOD loading in bleach plant filtrates for enhanced ECF technologies

Process	**Untreated bleach plant fitrates** (kg/ADMT)	**Treated bleach plant filtrates** (kg/ADMT)
Traditional ECF	15.00	1.20
Enhanced ECF (EC)	11.00	0.88
Enhanced ECF (EC + OD)	6.00	0.48

c) Low-Effluent ECF and TCF Bleaching

BOD loadings for low-effluent bleaching processes demonstrate the effect of increased bleach plant filtrate recirculation on the BOD levels of untreated bleach plant effluent. **Table 7** contains BOD loadings in the untreated bleach plant effluent for six mills: three have ECF bleaching sequences preceded by oxygen delignification, one has an ozone ECF sequence and two have TCF sequences with different levels of filtrate recirculation.[84] BOD levels decrease with the decrease in effluent flow. Secondary treatment has the largest impact on the BOD loading in the final bleach plant effluent, although decreasing the amount of BOD going into the treatment plant allows mills to increase production capacity without increasing the size of the effluent treatment system.

Table 7 AOX, BOD, COD and color loading in bleach plant filtrates from the six mill study

		Enhanced ECF			**Low-effluent ECF**	**TCF**	**Low-effluent TCF**
		Mill A [1]	Mill B [2]	Mill C [3]	Mill D [4]	Mill E [5]	Mill F [6]
Pollutant	**Units**	O-DE$_{O}$D	O-DE$_{OP}$DE$_{P}$D	O-DE$_{OP}$DE$_{P}$D	O-ZE$_{O}$D	O-QPPP	O-QPPPS
Production-Normalized Flows	m^3/ADMT	16.8	26.5	25	11.0 (9.4)	30.2	6.76
AOX	kg/ADMT	0.43[a]	0.98	0.46	0.08 (0.05)	< 0.01	< 0.01[b]
BOD$_5$	kg/ADMT	26.9[a]	-	-	6.94 (4.4)	-	2.91
COD	kg/ADMT	-	42.2	32.0	10.7 (11.0)	17.0	8.9
Color	kg/ADMT	46.8[a]	29.0	19.7	5.8 (3.1)	2.0	4.2
TCDD	pg/L (ppq)	ND[c]	ND[c]	ND[c]	ND[c]	[d]	ND[c]
TCDF	pg/L (ppq)	ND to 18	[d]	ND[c]	ND[c]	ND[c]	ND[c]

Notes: [a] Combined mill effluent into treatment system
[b] Detected on 1 of 4 days.
[c] Limit of detection is 10 ppq.

[d] Detected, but results are being reevaluated
[1] Mill A produces 82 ISO brightness pulp from a low kappa pulp
[2] Mill B produces high brightness pulp from a high kappa number pulp
[3] Mill C uses low kappa pulp
[4] Mill D recirculates the filtrate from the alkali extraction, and oxygen stages and purges some filtrate from the ozone stage. Numbers in parentheses are Union Camp's long-term averages.
[5] Mill E produces low kappa pulp and sewers all of the effluent
[6] Mill F recirculates 70% of its effluent

Source: Betsy Bicknell, Douglas Spengel, and Thomas Holdworth, "Comparison of Pollutant Loadings from ECF, TCF and Ozone/Chlorine Dioxide Bleaching," *Proceedings of the 1995 International Non-Chlorine Bleaching Conference* (San Francisco: Miller Freeman Inc., March 1995), 16. Wells Nutt, president, Union Camp Technologies Inc., letter to Harry Capell, Johnson & Johnson, 11 July 1995, 7.

2. Chemical Oxygen Demand (COD) and Color

Chemical oxygen demand is the amount of oxidizable compounds present in water. The COD of treated mill effluent represents the fraction of the substances in an effluent that the natural ecosystems cannot readily degrade, but provides no indication whether these substances are harmful.[85] COD does provide useful information about the sublethal toxicity of ECF and TCF effluents, but the source of COD within the pulp mill provides the most pertinent information.[86] The European Environmental Research Group has performed model ecosystem studies on pulp mill effluents since 1982 that include up to 54 different parameters. They developed a "response index" that summarizes the results of a model ecosystem test on a scale of 1 to 5, where higher numbers correspond to increased effects. Folke examined the relationship between the response index and COD loading for 14 effluents. He has found that the response index increases with the COD loading in the effluent.[87]

Color measures the large complexes of extracted organic matter from wood.[88] It also is influenced by the presence of metallic ions (e.g., iron and manganese) and humic matter. For kraft pulp and paper mills, most of the effluent color is attributable to losses of pulping liquor (black liquor) and bleach plant extraction stage filtrates.[89]

Although color is currently regulated by EPA and states as an aesthetic property, under certain conditions color may interfere with aquatic life by limiting light transmittance. Recent studies of effluent color below bleached kraft mills, however, suggest that it is unlikely that light transmittance is being reduced to a degree that would harm downstream aquatic communities.[90] Other studies, based a limited number of kraft mill effluents, have found that the source of much of the color measured in these effluents accounts for the responses in several marine bioassays.[91]

a) Traditional ECF Bleaching Processes

Tsai and his colleagues studied the impact of different levels of chlorine dioxide substitution on COD, color and AOX for softwood kraft pulp that has been pulped in a traditional digester. This pulp was bleached in the laboratory with levels of chlorine dioxide substitution that ranged from 70-100% with different total charges of bleaching chemicals. The COD loading of the bleach plant filtrates ranged from 62 - 73 kg/ADMT while the color loading ranged from 84 - 132 kg/ADMT.[92] Tsai reports that while increasing chlorine dioxide substitution from low levels of substitution (< 20%) to high levels (> 50%) decreases the color in bleach plant effluent, "increasing the substitution from 70% to 100% has only a marginal effect on effluent color."[93]

b) Enhanced ECF Bleaching Processes

Reducing the amount of lignin in the pulp exposed to chlorine dioxide in the first bleaching stage decreases both the COD and color loading in untreated bleach plant effluent. We present estimates from Weyerhaeuser[94] and International Paper[95] of the effect of installing extended delignification and oxygen delignification on treated bleach plant effluent in **Table 8**.

Table 8. COD and color loading in bleach plant filtrates from mills with enhanced ECF technologies

Process	**Weyerhaeuser [1]**		**International Paper**	
	COD (kg/ADMT)	**Color** (kg/ADMT)	**COD** (kg/ADMT)	**Color** (kg/ADMT)
Traditional ECF	40	110	29	95
Enhanced ECF (EC *or* OD)	30	90	21	72
Enhanced ECF (EC *and* OD)	15	45	12	40

[1] Values are approximate.

Tsai[96] and Folke[97] report a strong correlation between the percentage of lignin in the pulp and the COD loading in bleach plant effluent; Tsai confirms Weyerhaeuser's correlation of COD and color in bleach plant effluent.[98]

c) Low-Effluent Bleaching Processes

Low-effluent ozone ECF and TCF mills recirculate more of their bleach plant filtrate to the chemical recovery system than do mills with enhanced ECF processes. As with BOD loading in untreated bleach plant effluent, COD loading in the untreated bleach plant effluent as shown in **Table 7** decreases as the magnitude of the effluent flow decreases. The low-effluent ECF and TCF mills have the lowest COD releases of the six softwood bleached kraft mills. Maples and his colleagues estimate that BFR™ technology will achieve similar results for COD and color as the ozone ECF mill in the six mill study.[99]

The six mill study suggests that the combination of bleaching chemicals may also affect the COD loading in the bleach plant effluent at ECF and TCF mills. According to Bicknell and her colleagues, "Mill E, which bleaches with peroxide, sewers all effluent and has a production-normalized flow slightly higher than Mills B and C, yet Mill E discharges approximately half the COD loading as the two ECF mills."[100] The difference in the color loading of these mills is also large. The color loading of 1.97 kg/ADMT from Mill E is 4% of the average color loading in the bleach plant effluents of Mills B and C.

3. Adsorbable Organic Halogens (AOX)

AOX is a summary parameter that measures the approximate amount of chlorine (and other halides) present in organic material that adsorbs to activated charcoal; thus, AOX provides an estimate of the total amount of chlorinated organic material in the effluent.

Note of caution: In the regulatory impact assessment of the proposed effluent guidelines, EPA states some of the issues associated with controlling AOX. "Although AOX concentrations can be used to determine the removal of chlorinated organics to assess loading reductions, they do not provide information on the potential toxicity of the effluent, and therefore, are not appropriate to evaluate the potential impacts on the environment. Although no statistical relationship has been established between the level of AOX and specific chlorinated organic compounds, AOX analysis can be an inexpensive method for obtaining the "bulk" measure of the total mass of chlorinated organic compounds."[101]

a) Traditional and Enhanced ECF Bleaching Processes

We present data on the AOX loading in the bleach plant filtrates of the base case, traditional ECF and enhanced ECF softwood bleached kraft pulp mills in **Table 9**. AOX loadings in the treated mill effluent decrease as chlorine dioxide substitution in the first bleaching stage increases, and when mills reduce the amount of lignin in the unbleached pulp before it enters the bleach plant. Tsai and his colleagues confirmed the correlation of AOX to both of these factors in their laboratory bleaching tests.[102]

Table 9. AOX loading in the bleach plant filtrates of softwood bleached kraft pulp mills

Process	**AOX (kg/ADMT)**
Base Case (50% chlorine dioxide substitution) [103]	1.8 - 2.2
Traditional ECF[104]	1.5
Enhanced ECF[105]	0.4 - 1.1

b) Low-Effluent Bleaching Processes

Table 7 shows the AOX loading in the untreated bleach plant effluent of the six mill study. According to Bicknell and her colleagues, "The bleach plant AOX loading at the ozone ECF mill is about one order of magnitude less than the AOX loading at the three chlorine dioxide ECF mills. The bleach plant AOX loading at the two TCF mills is reduced by another one or two orders of magnitude."[106]

4. Dioxins

The discussion of dioxin loading in bleached kraft mill effluent has two parts. The first part examines the dioxin loadings in the *treated mill* effluent for mills that have traditional ECF and enhanced ECF bleaching processes, and the dioxin loadings in the *bleach plant* effluent for mills with traditional ECF and ozone ECF bleaching sequences. The second part of the discussion explores whether ECF bleaching processes provide an acceptable level of safety from dioxin exposure for certain sensitive populations.

The U.S. industry reacted quickly when EPA found, in 1985, that bleached kraft mills discharged dioxins into their receiving waters. The 1993 NCASI survey of U.S. bleached chemical pulp mills showed that the U.S. industry had reduced the discharge of TCDD 90% from a mean final mill effluent loading of 51 ppq in 1988 to a mean loading of 5 ppq in 1993; the mean TCDF loading in the final mill effluent of 23 ppq represents a 95% decrease from the mean TCDF loading of 443 ppq in final mill effluent from 1988.[107] The mean loading counts loadings that were below the limit of detection at half the limit of detection; thus, for example, an effluent sample with TCDD below a detection limit of 10 ppq would be counted at 5 ppq.

In their proposed effluent guidelines, EPA requires the concentrations of TCDD and TCDF in the *bleach plant filtrates* of bleached kraft mills to be below the analytical detection limit of 10 ppq. The concentrations of dioxins will be higher in the bleach plant effluent than in the final effluent because, on average, the bleach plant effluent accounts for about one-third of the total effluent from a bleached kraft mill;[108] thus, the dioxin concentration of the untreated bleach plant effluent is a more sensitive measurement of the quantities of dioxins generated during the manufacture of bleached kraft pulp.

a) Traditional ECF Bleaching Processes

At a technical workshop sponsored by NCASI in February 1994, six mills presented data on dioxin concentrations in bleach plant effluent and treated mill effluent. While TCDD was not detected in the final effluent of bleached kraft mills using 50% chlorine dioxide substitution in the first bleaching stage at the detection limit of 10 parts per quadrillion (ppq), TCDF may be present in the final effluent of mills using as much as 90% chlorine dioxide substitution. James River, for example, reported that its mill in Wauna, OR found 20 parts per quadrillion (ppq) TCDD and 92 ppq TCDF in the bleach plant effluent at 50% chlorine dioxide substitution; no TCDD was found at the detection limit of 10 ppq, while concentrations of TCDF were 17 ppq in the final mill effluent.[109] International Paper reported similar results for the final effluent of one of its mills at 50% chlorine dioxide substitution for chlorine in the first bleaching stage.[110] At 70% chlorine dioxide substitution, TCDD was not detected in the bleach plant effluent at a detection limit 10 ppq, but 31 ppq TCDF were found in the bleach plant effluent and 17 ppq in the final effluent. At 90% chlorine dioxide substitution, the TCDF loading in the final effluent dropped slightly to 13 ppq. At 100% substitution, neither substance was detected in the final effluent at the Wauna, OR mill at a detection limit of 10 ppq.[111]

Solomon and his colleagues confirmed the reductions in the concentrations of TCDD and TCDF in the final effluent of mills that increased chlorine dioxide substitution from 50-70% to 100% in an analysis of publicly available data sent to regulatory agencies. The TCDD level in all but one of the analyses of final effluent was below a detection limit of 1-10 ppq for mills with traditional ECF bleaching. The mean and 95th percentile levels of TCDD in the final effluent of mills with 50-70% chlorine dioxide substitution were 4.1 and 27 ppq respectively. The mean and 95th percentile levels of TCDF of 15 samples of the final effluent of mills with 100% chlorine dioxide bleaching were 5.7 ppq and 25 ppq respectively, while the mean and 95th percentile TCDF levels in the final effluent of a similar number of samples from mills with 50-70% chlorine dioxide substitution were 19 ppq and 45 ppq respectively.[112]

b) Enhanced ECF Processes

A comparison of data from traditional and enhanced ECF softwood bleached kraft mills does not show conclusively that minimizing the lignin content in the unbleached pulp lowers the dioxin loading in the final effluent. The concentrations of TCDD are below detection limits of 0.8 to 4.2 ppq for all of the samples from all three mills. The mean TCDF loadings in treated mill effluent are 3.0 ppq for the mill with the enhanced ECF bleaching process[113] and 4.1 and 9.4 ppq for the two traditional ECF mills.[114] The means include loadings from the non-detectable samples at half the detection limit. Statistical analysis shows that the means are not significantly different. Additional sampling is required to confirm that mills with enhanced ECF processes have statistically lower TCDF concentrations in the treated mill effluent than do mills with ECF bleaching sequences. It is also possible that the test method cannot reliably quantify these low levels of TCDF. We present the TCDD and TCDF data from the three mills and the statistical analysis in **Table B-7** of Appendix B.

c) Ozone ECF and TCF Bleaching Processes

Much less data currently exists concerning the dioxin concentrations of ECF mills that replace chlorine dioxide with ozone in the first bleaching stage. **Table 7** contains data from the six mill study where Bicknell and her colleagues compare the TCDF loading in the bleach plant effluent of three enhanced ECF mills that use oxygen delignification, one ozone ECF and two TCF mills. "The three mills that do not use chlorine dioxide in the first bleaching stage generate bleach plant effluents free of detectable concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF. In contrast, 2,3,7,8-TCDF was detected in the bleach plant effluents from two of the three mills that used chlorine dioxide in the first bleaching stage."[115] Bicknell reported that the concentration of TCDF in bleach plant effluent of a mill with a low kappa bleaching sequence that produces pulp with a brightness of 82 ISO was above a detection limit of 10 ppq on 3 of 18 days of sampling. The maximum concentration was 18 ppq. TCDF also was found above a detection limit of 10 ppq in the bleach plant effluent of another mill with a low kappa ECF bleaching sequence, while TCDD was found above a detection limit of 10 ppq in the combined bleach plant effluent of a mill using a TCF sequence. The results from the latter two mills were surprising and are being reevaluated.[116]

Data from the James River mill supports the finding of the six mill study that detectable levels of TCDF may be present in the bleach plant effluent of mills that use chlorine dioxide in the first bleaching stage. Two of the eight samples of bleach plant effluent from a traditional ECF mill had TCDF concentrations above a detection limit that ranged from 1.8 to 10 ppq.[117]

d) Dioxins in the Environment

The correlation of the environmental loading of dioxins with the production of chlorinated organic substances in this century indicate that global dioxin contamination is primarily a contemporary development associated with anthropogenic activities.[118] According to Rappe, "The most significant known anthropogenic environmental sources include waste incineration, metals production, petroleum refining, and fossil fuel (petroleum and coal) combustion."[119] Dioxin emissions from bleached chemical pulp mills account for a small percentage of the *known* sources of dioxins released to the environment. The current estimate for total dioxin releases to the environment in the U.S. indicates that the pulp and paper industry's dioxin releases account for 3.1% of the known releases to air, water, land and product. Pulp and paper manufacturing accounts for all of the dioxins released to water.[120]

In calculating the background dioxin exposure levels for the general U.S. population, EPA estimated that the ingestion of beef and veal, dairy products, and milk account for 31.2%, 20.3% and 14.8% of the total background level, respectively. Cattle ingest dioxins as they eat grass that has been contaminated with dioxins from atmospheric deposition. Historically, bleached pulp mill effluent, however, has been the major source of the dioxin loading in fish tissue. Recent data from Maine's Department of Environmenton the dioxin loadings in fish from rivers downstream from pulp mills indicates that bleached kraft pulp mills may still be an important source in many areas.[121] One eight ounce meal per month of fish, which has an average dioxin concentration of 1.2 ppt, contributed 6.6% to the background exposure level.[122]

Fish comprises a significantly larger proportion of the diet of certain sub-populations such as Native Americans and subsistence and sports fishermen. EPA estimates that sports fishermen consume the equivalent of one eight-ounce meal per week, or 30 grams of fish per day.[123] The diet of certain Tribal members contains even larger quantities of fish. The Columbia River Inter-Tribal Fish Commission performed a survey with EPA of the fish consumption of the tribes of the Columbia River Basin. This study reported that the mean daily fish consumption for Tribal members was 58.7 grams per day.[124] Fish consumption is also an integral part of the Tribes' ceremonies. Sixty percent of the survey respondents reported consuming one to two six-ounce portions (approximately 170 to 340 grams/day),[125] a level far above EPA's assumption for fish consumption that is used to estimate the increased cancer risk from dioxin exposure. Recent research indicates that dioxin may impair mammalian immune and reproductive systems at even lower levels.[126] Thus, the current dioxin loading in fish may still be too high to provide an adequate margin of safety for these populations. Scientists and regulatory agencies in Canada and the U.S. continue to explore this issue.

C. Environmental Effects of Bleached Kraft Mill Effluents

This paper focuses on the sublethal effects of bleached kraft mill effluent because most treated effluents rarely are acutely toxic[127] to aquatic organisms in their receiving waters. Several researchers have compared the sublethal toxicity of ECF and TCF bleach plant and mill effluents using bioassays and model ecosystem studies. Sublethal effects include impaired growth, reproduction or immune response, effects that do not kill the organism but may decrease the population of that organism over time.

1. Studies of the sublethal toxicity of ECF and TCF bleach plant filtrates

a) Base Case, Traditional ECF and Enhanced ECF Filtrates

Little public information exists on the environmental effects of moving from the base case to traditional ECF bleaching. Weyerhaeuser[128] and Champion International[129] report reduced toxicity from their mill effluent when they converted the bleach plant from the base case to enhanced ECF bleaching with oxygen delignification. It is difficult, however, to attribute these reductions in effluent toxicity directly to the changes in the bleach plant effluent because mills make many additional changes during major modernizations. Most mills upgrade the brownstock washers when they install oxygen delignification or move to complete chlorine dioxide substitution. This improvement, for example, can mask the effect of specific changes in the bleach plant.[130]

In their laboratory study of different bleaching sequences, however, O'Connor and his colleagues compared untreated traditional and enhanced ECF bleach plant filtrates. They reported that filtrates from combined chlorine dioxide and alkali extraction stages from a traditional ECF bleaching sequence reduced water flea reproduction and fathead minnow growth more than did untreated bleach plant filtrates from the oxygen, 100%D and alkali extraction stages of an enhanced ECF bleaching process.[131] No whole mill effluent toxicity studies compare traditional ECF with enhanced ECF or TCF bleaching processes, because few mills installed 100% chlorine dioxide substitution before installing oxygen delignification, and no mill currently switches between traditional ECF and an enhanced ECF operation.

b) ECF and TCF Filtrates

Two studies that prepared the bleach plant filtrates in the lab reported that the untreated TCF filtrates exhibited higher levels of toxicity for a range of bioassays. There is little difference in the toxicity of the treated filtrates.

O'Connor and his colleagues at the Pulp and Paper Research Institute of Canada (PAPRICAN) studied the chronic toxicity of enhanced ECF and TCF bleach plant filtrates that they prepared in the laboratory. They tested the effects of these untreated filtrates on water flea reproduction and on fathead minnow growth. In both cases, they found that the effluent from the oxygen, chlorine dioxide and alkaline extraction stages of an ECF bleaching sequence with oxygen delignification caused the least toxic effects.[132]

Nelson and his colleagues tested laboratory-prepared treated enhanced ECF and TCF eucalyptus bleach plant filtrates with bioassays for plants, invertebrates and fish of importance to the Australian marine ecosystem.[133] These scientists found that the untreated TCF filtrates were much more toxic to all of the test species than the untreated enhanced ECF filtrates, with the exception of the shellfish where they showed similar toxicity. They also found a strong correlation between the toxicity of the TCF filtrates and residual hydrogen peroxide in the effluent.[134] These findings are consistent with those of O'Connor. Both groups used sodium meta-bisulfite to remove excess hydrogen peroxide from the TCF bleach plant filtrates; sodium meta-bisulfite, however, is also toxic to aquatic organisms at high concentrations. Lövblad and Malmström suggest that high concentrations of this substance may have been the source of the toxicity in the TCF filtrates of the O'Connor study. [135]

Nelson and his colleagues found that the treated enhanced ECF and TCF bleach plant filtrates showed similar toxicity to all species except the single-celled algae where the TCF effluent was more toxic. "While secondary treatment reduced toxicity, both of the enhanced ECF and one of the TCF effluents were still found to be toxic for sensitive sea urchin fertilization tests and scallop larval abnormality tests."[136]

Higashi and his colleagues have also observed the sensitivity of marine organisms to a component of effluent from bleach kraft mills. They analyzed different fractions of bleached kraft mill effluent and found that a large, highly-colored water soluble degraded lignin molecule exhibits most of the toxicity to sea urchin sperm, mollusk embryos, sole larvae and kelp sperm and eggs. [137] These researchers found that this "lignin derived macromolecule" acts at the cell surface to inhibit developmental events. This molecule binds to the heads of the sea urchin sperm and thus prevents fertilization of the egg. Studies suggest that treatment of the substance or bleached kraft mill effluent with reducing agents such as sodium meta-bisulfite effectively reduces the effect on sea urchin sperm.[138]

2. Studies of sublethal toxicity of bleached kraft mill effluents

Scientists have also studied the environmental effects of bleached kraft *mill* effluent. Researchers in Canada and Sweden have performed single species bioassays and model ecosystem tests to compare the toxicity of untreated and treated effluent from bleached kraft mills with enhanced ECF and TCF processes. Scientists at Environment Canada have been studying the effect of pulp mill effluent on the reproductive systems of the native fish species downstream from several pulp mills.

a) Studies of Enhanced ECF and TCF Bleached Kraft Mill Effluents

Studies of effluents from mills that use oxygen delignification and extended delignification to produce ECF and TCF pulps suggest that the environmental effects of these processes are low and similar. Model ecosystem studies confirm the single species bioassay studies performed on mill effluent.

Lövblad and Malström performed sublethal toxicity tests on untreated enhanced ECF and TCF effluents from Södra Cell's mills.[139] They found that the exposure to TCF effluents resulted in less growth inhibition of *Selenastrum* algae and less inhibition of zebrafish and fathead minnow reproduction than did the enhanced ECF effluents. Both the undiluted, untreated enhanced ECF and TCF effluents showed no inhibition of water flea reproduction at the most sensitive level, the No Observable Effect Concentration.[140]

Kovacs and his colleagues compared the bleach plant effluent from a Finnish mill that switched between enhanced ECF with oxygen delignification and ozone TCF bleaching.[141] They performed five bioassays: fathead minnow survival and growth, water flea survival/reproduction, *Selenastrum* (algae) growth, sea urchin fertilization and rainbow trout liver enzyme induction (EROD). In all cases, the treated TCF effluent had the least effect.

While a range of single species bioassay tests show TCF mill effluent to be less toxic than enhanced ECF mill effluent, model ecosystem studies do not show large differences in the environmental effects of enhanced ECF and TCF bleaching of unbleached kraft pulps. Kovacs reported that the model ecosystem studies showed no toxic effects from either effluent at concentrations that ranged from 0.05-0.25%.[142] Lövblad reported similar "response factors" from model ecosystem studies of bleach plant effluents for ECF and TCF bleached kraft mills that have extended delignification and oxygen delignification.[143] He notes that "when comparing ECF- and TCF-technology on an equal development level (i.e. with kappa number about 10 or lower before bleaching), we today know that the differences in, for example, the effluent toxicity is small and may be of limited ecological significance."[144] Scientists continue to collect information about the toxicity of ECF and TCF effluents.

b) Studies of the Effects of Pulp Mill Effluent on Native Fish Populations

The low toxicity of the effluents from mills with ECF or TCF bleaching and oxygen delignification and extended delignification suggests that the bleaching process does not generate many substances that adversely affect the organisms in mill receiving water ecosystems. Researchers at Environment Canada have found that pulp mill effluent affects the reproductive system of fish downstream from these mills. Laboratory studies have shown that plant sterols can decrease sex hormone levels and thus, might lead to these effects. EPA scientists in Gulf Breeze, FL have found that exposure to microbially degraded plant sterols causes female mosquitofish to exhibit male sexual characteristics.

Hodson and his colleagues reported that "field studies of natural fish populations have demonstrated that fish downstream of pulp mills show chemical contamination, induction of enzymes that metabolize xenobiotics, physiological changes indicative of impaired stress responses, impaired sexual maturation, reduced reproductive capability, changes in energy metabolism, pathology, changes in population demographics and recruitment and shifts in community structure."[145] Munkittrick and Van der Kraak reported that most of the population changes in wild fish at Jackfish Bay can be correlated with decreased levels of sex steroids in the blood. Secondary treatment and greater dilution of non-toxic effluent do not eliminate these responses at some sites.[146] These reproductive system effects were seen in fish downstream from a mill with oxygen delignification, partial chlorine dioxide substitution and secondary effluent treatment and downstream from mills that do not produce bleached pulp.

Schryer and his colleagues report that sex steroid levels in longnose suckers on the Wapiti River downstream from the Weyerhaeuser Canada Grande Prairie, Alberta mill showed no correlation with exposure to treated bleached kraft mill effluent, and that exposure to the effluent has had no population level effects on the wild fish on the Wapiti River.[147] Exposure to kraft pulp mill effluent only delays sexual maturation, it has no effect on the fertility of sexually mature fish, so one would not necessarily see population level effects in all cases.

Three factors may attenuate the delayed sexual maturation and other reproductive effects in the fish in the Wapiti River. First, there are no dams on the Wapiti River to keep these migratory fish from moving upstream of the mill, so their exposure to the effluent would be highly variable over time.[148] Second, nutrient enrichment at downstream sites in the river can mask the effect of exposure to bleached kraft mill effluent. Fish at downstream sites in a river are larger and reach sexual maturity earlier than do fish that live further upstream.[149] Third, the Grande Prairie mill installed reclamation systems to recover process spills during its 1992 modernization program. Black liquor spills from mill upsets are contained and reprocessed through the evaporator system.[150] Reducing black liquor spills can have a large effect on the toxicity of treated mill effluent because the black liquor and the effluents from the first chlorine or chlorine dioxide stage and the alkali extraction stage of the bleach plant are the most potent effluent streams within a modernized bleached kraft mill.[151]

Laboratory studies have linked exposure to β-sitosterol, a common plant sterol, to the reduced blood levels of sex steroids in fish. Van der Kraak found a dose-response relationship between depressed testosterone levels in male goldfish and the β-sitosterol concentration in water.[152] The lowest β-sitosterol concentrations from this study are similar to the concentrations found in receiving waters downstream from mills with affected fish populations.[153] Zacharewski and his colleagues tested black liquor with a sensitive bioassay for estrogenic compounds. These scientists note that estrogenic plant sterols, such as β-sitosterol, are likely candidates to cause the observed estrogenic activity.[154] Demonstrating that this substance impairs the reproductive systems of the wild fish downstream from pulp mills, however, requires additional research.

Davis and his colleagues found female mosquitofish with male sexual characteristics on a small stream downstream from kraft pulp mills in Florida. Davis reproduced the effect of exposure to kraft mill effluent by exposing female mosquitofish to a mixture of microbially degraded plant sterols that included β-sitosterol.[155] Treatment of the effluent reduces the extent of the masculinization. Removing the fish from exposure to the effluent stops the masculinization and aggressive behavior associated with male mosquitofish. Masculinized females that have been removed from the field have given birth to normal female offspring, but based on observations of "highly" masculinized females, Davis "strongly suspects that reproductive function becomes impaired, if not entirely lost, after continued KME [kraft mill effluent] exposure."[156]

The major source of plant sterols is spent liquor from the pulping process. Davis reports that tall oil, a by-product of kraft pulping, is composed of 20-25% resin acids, 46-48% fatty acids and 25-35% plant sterols.[157] The bleach plant is not an important source of plant sterols. Good brownstock washing and increased filtrate recirculation to the chemical recovery system will reduce the concentration of plant sterols entering the bleach plant where chlorine dioxide effectively oxidizes sitosterol in the bleach plant filtrates. Ozone also oxidizes the sitosterol, although the author did not quantify its effectiveness. Hydrogen peroxide appears to be a less effective oxidizing agent.[158] This finding indicates that mills that produce peroxide TCF pulps should minimize the amount of lignin in the unbleached pulp to reduce the levels of sitosterol in the bleach plant filtrates.

D. Summary

Effluent Quality:

BOD, COD and color [Sections V. B.1 and V. B.2]:

- **Moving to traditional ECF bleaching from 50% chlorine dioxide substitution has no observable effect on the magnitude of these effluent parameters.**

- **Using extended delignification and/or oxygen delignification to reduce the amount of lignin in the pulp before it enters the bleach plant reduces the loading of BOD, COD, and color in bleach plant filtrates.**

- **Installing low-effluent ECF or TCF processes decreases the loadings of all three effluent parameters to the lowest level of the options considered.**

AOX [Section V. B.3]:

- **The mean AOX loading in the softwood bleach plant filtrates with traditional ECF bleaching is about 25% lower than that of the base case.** Increasing the chlorine dioxide substitution in the first bleaching stage reduces the mean AOX loading in the bleach plant filtrates to 1.5 kg/air-dried metric ton (ADMT) of pulp from a loading of about 2.0 kg/ADMT in the bleach plant filtrates of the base case mill.

- **The mean AOX loading in treated softwood bleached kraft mill effluent of a mill with enhanced ECF bleaching is about 63% lower than the mean loading in the bleach plant filtrates of the base case.**

- **Recirculating the bleach plant filtrate from the alkali extraction stage to produce low-effluent ECF pulps reduces the AOX loading in the treated mill effluent to the lowest level of the ECF options considered.**

- **The AOX loading of TCF bleach plant filtrates is at background levels and is the lowest of the manufacturing technologies considered.**

Dioxins [Section V. B.4]:

- **Increasing the chlorine dioxide substitution from 50%-100% in the first bleaching stage reduces the concentrations of both TCDD and TCDF in treated bleached kraft mill effluent below the analytical detection limit of 10 ppq.**

- **The variability of the data cloud the effect of installing oxygen delignification or extended delignification on the dioxin loading in the treated final effluent of bleached kraft mills with ECF bleaching sequences.** Data show that the mean loading of TCDF in final effluent from enhanced ECF mills is lower than that from traditional ECF mills; however, statistical analysis indicates that these means are not statistically different. Current analytical methods are not sensitive enough to measure these dioxin loadings precisely. Additional research is required to determine whether installing oxygen delignification or extended delignification lowers the TCDF loading in the final effluent.

- **Mills that replace chlorine dioxide with ozone in the first bleaching stage may not generate dioxins.**

Effluent toxicity studies - Bleach plant filtrates [Section V. C.1]:

- **A Canadian laboratory study showed that filtrates from both traditional and enhanced ECF bleaching processes were less toxic to water flea reproduction and fathead minnow growth than were filtrates with 50% chlorine dioxide and 50% elemental chlorine.**

- **This study also showed that bleach plant filtrates from an enhanced ECF bleaching process had fewer chronic toxic effects to water fleas and fathead minnows than did filtrates with traditional ECF bleaching.**

- **Two studies of laboratory-prepared filtrates from enhanced ECF and TCF processes indicated that the untreated TCF filtrates were more toxic to several freshwater and marine organisms than were untreated ECF filtrates. The differences in the sublethal toxicity of treated ECF and TCF filtrates is small.** Excess hydrogen peroxide or sodium meta-bisulfite used to neutralize the peroxide may account for the toxicity of the TCF filtrates.

- **A large, highly colored, water soluble, degraded lignin molecule found in bleach plant effluent is toxic to the early life stages of marine plants, invertebrates and fish.**

Effluent toxicity studies - Mill studies [Section V. C.2]:

- **The results from current studies comparing ECF and TCF bleach plant filtrates from mills that bleach pulp with similar lignin content show little difference in chronic toxicity.** While a range of single species bioassays show that treated TCF mill effluents are less toxic than treated ECF mill effluents, model ecosystem studies do not show significant differences in the effluent from mills with similar pulping technologies.

- **Recent research suggests that exposure to compounds in the black liquor may reduce the reproductive capacity of wild fish downstream from bleached kraft mills. Laboratory research suggests that plant sterols may account for these effects.**

VI. SOLID WASTE GENERATED BY BLEACHED KRAFT MILLS

A. Scope

In this section we examine the quantity of solid waste generated by bleached kraft mills. Moving to the effluent-free bleach plant may increase the amount of material that is discharged as solid waste. The quality of the components of the solid waste stream also determine the disposal methods available to the mill.

1. Solid Waste Quantity

Bleached kraft mills generate five types of solid waste: unburned wood yard waste, wastewater sludge; ash from the recovery and power boilers; solid residuals from the chemical recovery system; and general mill refuse.[159] While some of these residues provide energy to operate the mills, the rest must be disposed of in an ecological and economical manner. Currently, primary and secondary sludge from wastewater treatment systems account for the largest portion of the solid waste stream.[160]

The quantity of solid waste generated by bleached kraft mills should not increase until mills operate their bleach plants with almost no effluent discharge. Mills with low-effluent bleaching processes concentrate metals and other non-process elements and purge them in the effluent. Estimates of the impact of effluent-free bleach plant operations vary. Experts at Champion International and Union Camp expect the increase in solid waste to be small.[161] Mannisto and his colleagues estimate that the amount of solid waste generated by an effluent-free bleached kraft mill where the bleach plant filtrate and the pulping liquor are sent to the chemical recovery system to be 2.5 to 3 times that of currently operating mills.[162]

B. Solid Waste Quality

The composition of the solid waste stream determines the disposal options available to bleached kraft mills. Mills that move to either traditional ECF or enhanced ECF processes will have to dispose of wastewater sludge. As mills approach the effluent-free bleach plant, the disposal of metals and other non-process elements that enter the pulp mill with the wood will become more problematic. Mills that operate effluent-free ECF bleach plants with separate recovery of the bleach plant filtrate will have to incinerate or otherwise treat chlorinated material, both organic and inorganic, in the residue from the filtrate evaporators.

1. Wastewater sludge

Clarifiers used *before* biological treatment generate primary sludge as gravity or flotation thicken the organic and inorganic materials suspended in the untreated mill wastewater. Primary sludge contains wood fibers as the principal organic component, and inorganic materials such as clay, calcium carbonate, titanium dioxide, inert solids rejected during the chemical recovery process, and ash. Bleach plant effluent generally bypasses the primary treatment system because of its low suspended solids content.

Clarifiers are used *after* biological treatment to remove biological solids in the treated effluent generate secondary sludge. Mills with activated sludge treatment systems generate most of the secondary sludge. Mills with aerated lagoons do not clarify the treated effluent, although they do generate some sludge when they dredge the lagoon. The solids in secondary sludge are mostly organic and contain bacterial and other microbial biomass.[163] Mills usually generate larger quantities of primary sludge.[164] Most mills dispose of the wastewater sludge in landfills, 27% of U.S. mills incinerate wastewater sludge, 8% of U.S. mills land-spread their sludge, and an additional 8% use other disposal methods. [165]

Installing traditional ECF or enhanced ECF processes may facilitate sludge incineration by reducing the combustion temperatures required to destroy the chlorinated organic compounds present in the sludge. Wastewater sludge from mills with TCF bleaching should have very low concentrations of both organic and inorganic chlorides.

The dioxin loading in bleached kraft mill wastewater sludges affect the ability of mills to landspread sludge. EPA and the American Forest & Paper Association (AF&PA) developed a voluntary industry environmental stewardship program for the land application of sludge.[166] Sludges with less than 10 ppt TEQ of TCDD are subject to reduced monitoring and reporting requirements and can be applied to land at appropriate agronomic rates. Sludge with up to a maximum TCDD concentration of 50 ppt TEQ can be land applied, but the concentration of dioxin in the soil cannot exceed 10 ppt TEQ. Sludge may be applied to land used for grazing domestic animals for human consumption only if the resulting TCDD/TCDF soil concentration is less than 1 ppt.

This industry/EPA program should provide adequate protection from dioxin-related health effects in wildlife. A 1987 industry study of the effect of applying sludge with a TCDD concentration of 10.8 ppt and a TCDF concentration of 106 ppt on birds, deer mice and invertebrates that inhabit forested areas in Wisconsin found that the concentrations of dioxins increased in both the deer mice and the birds However, no dioxin-related toxic effects were observed in the populations of deer mice or birds on these plots.[167]

Three recent studies present data on the dioxin loading in wastewater sludge for bleached kraft mills. In the short-and long-term studies of 14 bleached kraft mills, EPA found TCDD above a detection limit of 1 ppt in 9 of the mills with a maximum loading of 67 ppt. Sludges from 12 of the 14 mills contained TCDF loadings above a detection limit of 1 ppt with a maximum loading of 160 ppt. [168]

In the 1993 NCASI survey of 97 chemical pulp mills reported mean TCDD and TCDF concentrations in wastewater sludge of 11 ppt and 49 ppt respectively, and maximum concentrations of 133 ppt and 735 ppt.[169] Mills used a protocol similar to that of the EPA 104 mill study, rather than reporting concentrations based on their own test protocols.[170] TCDF has a TCDD toxic equivalence factor of 0.1, so the mean concentration in chemical pulp mill sludge in 1993 was 15.9 ppt TEQ.

Dioxin loading in mills with ECF bleaching are much lower than the current average loading of chemical pulp mills. In the six mill study, TCDD was found at the detection limit of 1 ppt in 2 of 12 samples of primary sludge of a mill that uses ECF bleaching with oxygen delignification. TCDF was detected in 10 of the 12 samples with a range of 2 ppt to 7 ppt. The limit of detection for TCDF in the sludge was 1 ppt.[171]

Little published data currently exist on the quality of wastewater sludge from TCF bleached kraft mills. Bleached kraft mills, however, that have installed TCF bleaching sequences have eliminated dioxin formation during the pulp manufacturing process, so the dioxin loading in the sludge should not constrain the land-spreading of sludge from these mills.

2. Solid waste quality of effluent-free bleach plants

The composition of solid waste from a mill with low-effluent ECF or TCF bleaching processes that sends bleach plant filtrate to the chemical recovery system does not change appreciably until almost all of the bleach plant filtrate is recirculated. When these mills operate effluent-free bleach plants, metals and other non-process elements probably will be removed in the chemical recovery system and thus increase the solid waste generated. Mills may also have to handle increased amounts of recovery boiler ash. Some of the waste from the chemical recovery system may be considered hazardous and the boiler ash may be difficult to manage because of its water solubility.[172] Mills that recover the filtrate from an ECF bleach plant using a separate recovery system will have to manage evaporator residue with a high concentration of both organic and inorganic chlorides, and dispose of the ash if the residue is incinerated. The ash may contain dioxins that form in the presence of fly ash, flue gases and chlorides.[173]

C. Summary

- **Installing traditional ECF, enhanced ECF or low-effluent bleaching processes reduce the loading of chlorinated organic compounds and dioxins in wastewater sludge.**

- **Engineers predict that for mills with effluent-free bleach plants that recirculate the bleach plant filtrate to the chemical recovery system, the quantity of solid waste generated will increase. Additional research is needed to determine whether some of these wastes will be hazardous or difficult to dispose.**

- **Mills that send filtrate from ECF bleach plants to a separate recovery system may have to dispose of ash if the mill incinerates the organic waste. Additional research is needed to determine whether the resulting ash contains dioxins, and thus needs to be handled as hazardous waste.**

VII. EXPLANATION OF KEY TERMS AND ABBREVIATIONS

Note: Terms listed and defined below are in **boldface.** Terms which may be of particular interest to the reader in a given context, but are not listed below, are in *italics.*

Acute toxicity tests of the effluent measure the concentration that results in the death of a set percentage of test organisms over a specified period of exposure. A widely used test of acute toxicity determines the effluent concentration that results in the death of 50% of the organisms in either 48 or 96 hours.

Adsorbable organic halogens (AOX): Measure of the total amount of halogens (chlorine, bromine and iodine) bound to dissolved or suspended organic matter in a wastewater sample. For pulp, paper and paperboard wastewaters, essentially all of the organic substances measured as AOX are chlorinated compounds that result from the bleaching of pulps with chlorine and chlorinated compounds such as chlorine dioxide and hypochlorite. AOX provides information about the quantity of chlorinated organic compounds in wastewater, and thus contains a broad mix of compounds that have different chemical properties. The actual composition of AOX in pulp mill **effluent** varies from mill to mill, depending on the wood species used and the process parameters.

“Although AOX concentrations can be used to determine the removal of chlorinated organics to assess loading reductions, they do not provide information on the potential toxicity of the effluent, and therefore, are not appropriate to evaluate the potential impacts on the environment. Although no statistical relationship has been established between the level of AOX and specific chlorinated organic compounds, AOX analysis can be an inexpensive method for obtaining the ‘bulk’ measure of the total mass of chlorinated organic compounds.” (U.S. EPA, *Regulatory Impact Assessment of Proposed Effluent Guidelines and NESHAP for the Pulp, Paper and Paperboard Industry*, (Washington: Office of Water, EPA-821-R93-020, November 1993), pp. 7-25 - 7-26)

AF&PA: The American Forest & Paper Association.

Air-dried metric tons (ADMT): Pulp with 10% water content by weight. One ADMT is equivalent to 0.9 **oven-dried metric ton of pulp** (ODMT).

Air-dried tons of final product (ADTFP/ADMTFP): Tons or metric tons of final product made at a mill.

American Forest & Paper Association: The trade association for the U.S. pulp, paper and forest products industry.

Anaerobic: Biochemical process or condition occurring in the absence of oxygen.

Anthraquinone: Chemical added to the **digester** that increases the amount of lignin removed from **kraft pulp** while maintaining its strength.

Ash: Inorganic matter present in the paper sheet, such as **clay** or **titanium dioxide**.

Bioassays test the toxicity of an effluent on single species of plants, invertebrates, or fish that represent the classes of organisms present in mills' receiving water ecosystem. Scientists expose these organisms to different concentrations of the effluent in the laboratory to measure acute and sublethal toxic effects.

Biochemical oxygen demand (BOD): Amount of oxygen required by aerobic (oxygen-requiring) organisms to carry out normal oxidative metabolism or the amount required by oxidation of metabolic by-product from **anaerobic** organisms in water containing organic matter. Thus, BOD measures the amount of dissolved organic material that is degraded naturally once it enters a mill's receiving waters. For regulatory purposes, BOD is most often measured over a five-day period in the United States. The BOD in a test bottle can consume oxygen well in excess of 100 days, and the five-day test may capture only 50-75% of the total BOD.

Black liquor: Spent, **lignin**-rich **cooking liquor** generated in the **kraft pulping** process.

Bleached chemi-thermomechanical pulp: A stronger and brighter variation of **chemi-thermomechanical pulp (TMP)**, a pulp that reduces energy consumption for certain paper grades by combining thermal pretreatment with chemical methods.

Bleaching: Chemical treatment of pulp fibers for the purpose of: (1) increasing pulp **brightness**, (2) improving cleanliness by disintegrating contaminating particles such as bark, and (3) improving brightness stability by reducing the tendency of bleached pulp to turn yellow. Bleaching removes residual **lignin** chemicals..

Brightness: Light-reflecting property of paper or pulp. Brightness measurements compare paper and pulp with a reference standard (measured on a scale of 1 to 100 where 100 represents the reflectance of magnesium oxide). Bleached **kraft pulps** range in brightness from the low 80s to over 90. Unbleached **mechanical pulps** range from 55 to 62.

Capacity: The amount of pulp, paper or paperboard that a paper machine or mill is capable of producing over an extended period of time with the full use of its equipment, adequate raw materials and labor and full demand for its products. Capacity is often slightly higher than actual production.

Carbon dioxide (CO_2): Greenhouse gas associated with global climate change that results from the complete combustion of biomass and fossil fuels.

Cellulose: Polymer of sugar units that forms transparent, hollow and flexible tubes. It is the most abundant natural polymer produced by plants.

Chelating stage refers to the stage that usually proceeds hydrogen peroxide bleaching. Chelating agents tie-up metals so that they can be washed out of the pulp. These metals would otherwise react with the hydrogen peroxide and destroy it.

Chemical oxygen demand (COD): Amount of oxidizable compounds (composed of carbon and hydrogen) present in the water. Since an **effluent**-treatment system removes most of the organic material that would be degraded naturally in the receiving waters, the COD of the final effluent provides information about the quantity of more persistent substances discharged into the receiving water.

Chemical pulp: Pulp produced from wood that has been cooked with various chemicals; used to produce many grades of printing papers and some paperboard grades, such as **SBS**.

Clarifier: Process water storage tank in which suspended solids are allowed to settle.

Clean Air Act: Federal statute that gives the U.S. Environmental Protection Agency the authority to regulate emissions of air pollutants from all sources in the United States. The purpose of the statute is to protect and enhance the quality of the nation's air resources. 42 U.S.C. &&7401 to 7642.

Clean Water Act: Federal statute that gives the U.S. Environmental Protection Agency the authority to regulate discharges of pollutants from all sources into the waters of the United States. The purpose of the statute is to restore and maintain the chemical, physical and biological integrity of the nation's waters. 33 U.S.C. && 1251 to 1387.

Color: Used to describe colored wastewater discharge from **chemical pulping**, pulp bleaching or colored-paper manufacture. The wastewater is colored by the **lignin** and lignin derivatives present in spent **cooking liquors**.

Condensates refer to the water from the digester area and the water, liquor from the brownstock washers is concentrated before being fed into the recovery boiler. The condensates from the first evaporator is referred to as **foul condensates** because these condensates usually have higher concentrations of TRS compound and other organic substances dissolved in the weak black liquor. Clean condensates are generated in subsequent evaporator stages. This water is often reused at the mill.

Consistency: The percentage of **cellulose** fibers in a pulp **slurry,**.

Cook: To treat wood with chemicals, under pressure and/or extreme heat, to produce pulp for making paper and paperboard.

Cooking liquor: Chemical solution used to pulp wood.

Delignification: The process of removing **lignin** from wood or non-wood fibers.

Digester: Pressurized vessel in which wood chips are **cooked** to separate fibers from each other and to remove contaminants.

Dioxins: A group of persistent, toxic substances, including furans, that are produced in trace amounts when unbleached pulp is exposed to elemental chlorine. Term used to describe the families of chemicals known as chlorinated dibenzo-p-dioxins and dibenzo-p-furans. These families consist of 75 different chlorinated dibenzo-p-dioxins and 135 different chlorinated dibenzo-p-furans. These molecules can have from one to eight chlorine atoms attached to a planar carbon skeleton. 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF) are two of the most toxic members of this family of compounds. If dioxins are detected in the releases from bleaching processes that expose unbleached pulp to **elemental chlorine**, the dioxins are most likely to be TCDD and TCDF.

Effluent: Wastewater that has been discharged either to a sewer or to a stream or other body of water.

Elemental chlorine: Chlorine gas (Cl_2).

Elemental chlorine-free (ECF): Bleaching processes that substitute **chlorine dioxide** for **elemental chlorine** and **sodium hypochlorite** in the bleaching process.

Filtrate: Water that is either pressed or washed out of the pulp during the pulping and bleaching; once the water has been discharged to a sewer it becomes **effluent**.

Furans: See **dioxins.**

Hardwood: Technically, a dicotyledonous tree. Hardwoods typically have broad leaves and are often deciduous (they lose their leaves during winter); e.g., maple, oak, aspen, cherry and ash.

Hazardous air pollutant (HAP): One of 189 toxic substances as defined by the 1990 **Clean Air Act** amendments.

Hydrophilic: Affinity for water.

Hydrophobic: Aversion to water.

Kappa number is a measure of the amount of lignin remaining in pulp. One can estimate the percentage of lignin in a pulp using the following equation. A pulp with a kappa number of 18, for example, contains 2.7% lignin.

$$\% \text{ Lignin} = 0.15\% \times \text{Kappa number}$$

Kraft mill: Mill that produces **kraft pulp**.

Kraft pulp: Also called **sulfate pulp**. **Chemical pulp** made using an alkaline cooking process with sulfur compounds. This pulp can be **bleached** or **unbleached** and is noted for its **strength**.

Lignin: Complex organic material that binds together fibers in trees and woody plants.

Market pulp: Pulp sold on the open market; virgin market pulp is air-dried and wrapped; **deinked market pulp** can be sold in air-dried or wet-lapped (partially dry) form.

Nitrogen oxides (NO_x): Emissions that occur when fuels that contain nitrogen are burned. Most NOx forms at high temperatures from combustion of nitrogen in the air. Nitrogen oxides contribute to acid rain and can react with **volatile organic compounds** in the atmosphere to produce the ozone in photochemical smog.

Oven-dried ton/metric ton of pulp (ODTP/ODMTP): The **moisture content** of oven-dried pulp is zero. Air-dried pulps have about a 10% moisture content

Ozone (O_3): Powerful oxidizing agent used in bleaching processes to remove **lignin** and colored substances from pulp. Ozone is formed by passing electricity through a stream of oxygen gas. Low-level atmospheric ozone is a pollutant in smog that results from the reaction of **nitrogen oxides** and **volatile organic compounds** with sunlight.

Particulates: Small particles that are dispersed into the atmosphere during combustion.

Persistence: Ability of a substance to remain active over a period of time.

Pulp: **Cellulose** fiber material, produced by chemical or mechanical means, from which paper and paperboard are manufactured. Sources of cellulose fiber include wood, cotton, straw, jute, bagasse, bamboo, hemp and reeds.

Pulpwood: **Roundwood products**, **whole-tree** chips, or wood **residues** that are used for the production of wood **pulp**.

Purchased energy consumption: Amount of purchased electricity and fossil fuels that mills use to run the equipment and to generate process steam. Cogeneration and more efficient combustion of **lignin** and other wood waste decreases the purchased energy consumption of the mill.

Saltcake (sodium sulfate) is the chemical that is added to the recovery boiler to replace the sulfur lost in the pulping process. It is converted in the hearth of the recovery boiler to sodium sulfide, one of the components of white liquor. Carry-over of black liquor from the brownstock washers is often expressed in terms of kg of saltcake loss per metric ton of pulp.

Secondary treatment: **Wastewater treatment** systems that use microorganisms to convert the dissolved organic waste in the effluent into a more harmless form. Although primarily designed to remove **BOD**, secondary treatment also reduces the loading of **COD** and **AOX**.

Shrinkage: Decrease in dimensions of a paper sheet; weight loss between amount of pulp used and paper produced.

better surface properties and improve certain physical properties of a sheet. The papermaker generally applies either surface or internal sizing, which can be applied as sole treatments or in combination

Sodium hypochlorite: Bleaching chemical produced by mixing sodium hydroxide and **elemental chlorine**. Mills are eliminating this chemical from bleaching processes because it produces large quantities of **chloroform**.

Softwood: Coniferous usually evergreen tree that has needles or scale-like leaves; e.g., pine, Douglas fir and spruce.

Sublethal toxic effects describe effects that do not kill the organism, but may reduce the total population over time. These effects include reduced growth, and impaired reproductive or immune systems.

Sulfate pulp: See **kraft pulp**.

Sulfur dioxide (SO_2): Chemical compound produced when boilers burn fuel that contains sulfur. Of the fuels used in the paper industry, oil and coal generally contain the highest quantities of sulfur.

Suspended solids: See **total suspended solids**.

Total energy consumption: Energy, including electricity and all forms of fuels, consumed to produce a ton of pulp or paper.

Totally chlorine-free (TCF): Bleaching process that uses no chlorine-based chemicals.

Total reduced sulfur compounds (TRS): Mix of organic compounds that cause the odor associated with **kraft pulp** mills. These compounds include hydrogen sulfide, dimethyl sulfide, dimethyl disulfide and methyl mercaptan.

Total suspended solids (TSS): Amount of suspended solids in the **effluent**. They can eventually settle on the bottom of a mill's receiving water and affect the habitat of bottom-living organisms. Well-operated treatment systems remove most of these solids. Concern remains, however, because heavy metals, **dioxins** and other unchlorinated compounds can be adsorbed onto the remaining suspended solids.

Toxic equivalence (TEQ): The EPA uses toxic equivalence factors (TEFs) to estimate the relative toxicity of different members of the **dioxin** and **furan** families, because they produce similar toxic effects, but at different doses. E.g., TCDD is the most toxic member of the dioxin and furan family and is assigned a toxic equivalence factor of 1.0, while the less toxic TCDF is assigned a toxic equivalence factor of 0.10. Using these factors, the sum of the toxicity of one gram of TCDD and one gram of TCDF would be equal to 1.1 grams TEQ of TCDD.

Volatile organic compounds (VOCs): Broad class of organic gases, such as vapors from solvents and gasoline that react with nitrogen oxides in the atmosphere to form low-level atmospheric **ozone** .

VIII. APPENDICES

LIST OF WHITE PAPERS

Paper Performance

Functionality Requirements for Uncoated Business Papers and Effects of Incorporating Postconsumer Recycled Content (White Paper 1)

Functionality Requirements for Coated and Uncoated Publication Papers and Effects of Incorporating Postconsumer Recycled Content (White Paper 8)

Functionality Issues for Corrugated Packaging Associated with Recycled Content, Source Reduction and Recyclability (White Paper 6A)

Functionality Issues for Folding Cartons Associated with Recycled Content, Source Reduction and Recyclability (White Paper 6B)

Recycling and Used Paper Management

Economics of Recycling as an Alternative to Traditional Means of Solid Waste Management (White Paper 2)

Lifecycle Environmental Comparison - Virgin Paper and Recycled Paper-Based Systems (White Paper 3)

Economics of Manufacturing Virgin and Recycled-Content Paper (White Paper 9)

Forest Management

Environmental Issues Associated with Forest Management(White Paper 4)

Economic Considerations in Forest Management (White Paper 11)

Pulp and Paper Manufacturing

Environmental Comparison of Bleached Kraft Pulp Manufacturing Technologies (White Paper 5)

Economics of Kraft Pulping and Bleaching (White Paper 7)

Environmental Comparison - Manufacturing Technologies for Virgin and Recycled-Content Printing and Writing Paper (White Paper 10A)

Environmental Comparison - Manufacturing Technologies for Virgin and Recycled Corrugated Boxes (White Paper 10B)

Environmental Comparison - Manufacturing Technologies for Virgin and Recycled Coated Paperboard for Folding Cartons (White Paper 10C)

Comparison of Kraft, Sulfite and BCTMP Pulp and Paper Manufacturing Technologies (White Paper 12)

Nonwood Plant Fibers as Alternative Fiber Sources for Papermaking (White Paper 13)

LIST OF APPENDICES

Appendix A. List of panelists and reviewers for Issue Paper No. 5 and the draft White Paper No. 5

Appendix B. Environmental releases to air and water

A. Appendix A: Panelists and Reviewers of Issue Paper No. 5

Members of the Task Force gratefully acknowledge the time, effort and expertise that the panelists and reviewers provided to its research. The work and the final products of the Task Force are the sole responsibility of its members. The panelists and reviewers listed below have not endorsed the contents of these papers.

The expert panel on environmental comparison of bleached kraft pulp manufacturing technologies took place on September 21, 1994 at the offices of The Prudential in Newark, NJ.

Panelists:

John Carey
Director, Aquatic Ecosystem Conservation Branch, Environment Canada

*† **Gerard Closset**
Vice President - Technology, Champion International Corporation

*† **Roland Lövblad**
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*† **Dale K. Phenicie**
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† **Peter Washburn**
Staff Scientist, Natural Resources Council of Maine

The following reviewers provided comments on Issue Paper No. 5 and a draft of White Paper No. 5:

*† **E. Lee Andrews**
Senior Vice President, Fine Papers Division, Westvaco Corporation

† **Jessica Landman**
Senior Attorney, Natural Resources Defense Council

*† **Peter Lee**
Staff Vice President, Research & Development, International Paper Co.

* **Thomas McDonough, Ph.D.**
Associate Vice President, Research and Academic Affairs, Institute of Paper Science and Technology

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B. Appendix B: Additional Information on Releases to Air and Water

This appendix contains the emission factors for the air emissions from non-combustion process sources generated by bleached kraft mills. **Table B- 7** contains data on TCDD and TCDF concentrations in the final effluent of three softwood ECF bleached kraft mills.

Table B-1	Energy requirements to produce bleaching chemicals
Table B-2	Energy consumption to manufacture the bleaching chemicals for the different manufacturing processes
Table B-3	Hazardous air pollutant (HAP) emissions from bleached kraft mill process sources
Table B-4	Volatile organic compound (VOC) and total reduced sulfur (TRS) air emissions from bleached kraft mill process sources
Table B-5	Hazardous air pollutant (HAP) emissions from pulp and paper mill sources
Table B-6	Volatile organic compound (VOC) and total reduced sulfur (TRS) air emissions from pulp and paper mill sources
Table B-7	Dioxin loading (TCDD and TCDF) in the final effluent of three softwood ECF bleached kraft mills

Table 1. Energy requirements to produce bleaching chemicals

Bleaching chemical energy analysis

Conversion factors:

1 kWh	0.0105 million Btus
1 metric ton of steam	2.53 million Btus

Energy to produce one metric ton of chlorine dioxide with an R-8 process [1]

Input	**Quantity**	**Input Electricity**	**Input Steam**	**Chlorine dioxide Electricity**	**Chlorine dioxide Steam**
	(metric tons)	(kWh/metric ton)	(metric ton/metric ton)	(kWh/metric ton)	(metric ton/metric ton)
Sodium chlorate	1.7	5,600	0.0	9,667	0.0
Methanol	0.2	60	0.0	9	0.0
Sulfuric acid	1.0	100	0.0	100	0.0
Steam	1.0	0	4.8	0	4.8
Electricity	1.0	272	0.0	272	0.0
Total				**10,049**	**4.8**

Energy required to manufacture bleaching chemicals

	Electricity (kWh/metric ton	Steam metric ton/metric ton)	Electricity (mm Btu/ metric ton)	Steam (mm Btu/ metric ton)	**Total energy (mm Btu/ metric ton)**
Elemental chlorine (Cl_2)	1,400	0.0	14.7	0.0	**14.7**
Sodium hydroxide (NaOH	1,400	0.0	14.7	0.0	**14.7**
Oxygen (O_2)	400	0.0	4.2	0.0	**4.2**
Oxidized white liquor (OW	3,916	0.0	41.1	0.0	**41.1**
Hydrogen peroxide (H_20_2	1,720	6.6	18.1	16.7	**34.8**
Chlorine dioxide ($Cl0_2$)	10,049	4.8	105.5	12.1	**117.6**
Ozone (O_3)	12,518	0.0	131.4	0.0	**131.4**
Sulfuric acid (H_2SO_4)	100.0	0.0	1.1	0.0	**1.1**

Sources: [1] Wells Nutt, president, Union Camp Technologies Inc., letter to Lauren Blum, September 27, 1994 and letter to Harry Capell, 12 July 1995.
[2] Jean Renard, International Paper, personal communication, May 26, 1995;
[3] N. Peters and R.W. Cunnington, "Power Consumption and AOX: What's Going to Happen in Canada?" *Pulp & Paper Canada,* **95(5)**: 11 - 13 (1994).
[4] Paul Stockburger, "What you need to know before buying your next chlorine dioxide plant",

Table B-2. Energy consumption to manufacture the bleaching chemicals for the different manufacturing processes

$(C_{50}D_{50})$DED

Chemical	**Quantity**	**Electricity**	**Steam**
Chlorine, C	**40.0**	**0.6**	**0.0**
Chlorine dioxide,	15.4		
D1	26.0		
D2	9.5		
Total	**50.9**	**5.4**	**0.6**
Sodium hydroxid	42.0		
E2	5.0		
D1 buffer	16.0		
D2 buffer	6.0		
Total	**69.0**	**1.0**	**0.0**
Total		**7.0**	**0.6**

D(EO)DED

Chemical	**Quantity**	**Electricity**	**Steam**
Chlorine dioxide,	39.2		
D1	26.0		
D2	9.5		
Total	**74.7**	**7.9**	**0.9**
Sodium hydroxid	42.0		
E2	5.0		
D0 buffer	24.5		
D1 buffer	16.0		
D2 buffer	6.0		
Total	**93.5**	**1.4**	**0.0**
Oxygen, E1	**7.5**	**0.0**	**0.0**
Total		**9.3**	**0.9**

OD(EO)D

Chemical	**Quantity**	**Electricity**	**Steam**
Oxygen,O	25		
E1	7.5		
Total	**32.5**	**0.2**	**0**
Oxidized white liq	**40**	**1.6**	**0**
Chlorine dioxide,	13.5		
D2	8.0		
Total	**21.5**	**2.3**	**0.3**
Sodium hydroxide,	42.0		
D2 buffer	5.0		
Total	**47.0**	**0.7**	**0.0**
H2SO4, D1 buffer	**8**	**0.0**	**0**
Total		**4.8**	**0.3**

OZ(EO)DD

Chemical	**Quantity**
Oxygen, O	25
EO	5
Total	**30**
OWL	**40**
Ozone, Z	**7.35**
Sulfuric acid,	**25**
Chlorine dioxide	
D1	9.8
D2	6.6
Total	**16.4**
Sodium hydroxide	
Z	5
EO	5
D1 buffer	6.05
D2 buffer	4.1
Total	**20.15**
Total	

Units: Quantity = metric tons of chemical per oven-dried ton of bleached pulp
Electricity and Steam = Millions of Btu's per oven-dried ton of bleached pulp

Source: Wells Nutt, president, Union Camp Technologies Inc., letter to Harry Capell, Johnson & Johnson, 12 July 1995, 5-6.

Table B - 3. Hazardous air pollutant (HAP) air emissions from all sources at the mill

SOURCE	**Total HAPs** (lb/ODTP)	**Methanol** (lb/ODTP)	**Acetaldehyde** (lb/ODTP)	**Formaldehyde** (lb/ODTP)	**Methyl ethyl ketone** (lb/ODTP)	**n-hexane** (lb/ODTP)	**chloroform** (lb/ODTP)	**Methyl isobutyl ketone** (lb/ODTP)	**benzene** (lb/ODTP)	**styrene** (lb/ODTP)	**1,2,4, trichloro-benzene** (lb/ODTP)
PULPING											
Brownstock screening to vent	0.0180	0.0160	0.0000	0.0006	0.0002	0.0000	0.0001	0.0000	0.0000	0.0000	0.0001
Average emissions from brownstock washers	0.4853	0.4487	0.0183	0.0013	0.0044	0.0008	0.0017	0.0012	0.0001	0.0008	0.0006
Swd decker hood & filtrate tank vents	0.0820	0.0670	0.0012	0.0000	0.0054	0.0000	0.0002	0.0001	0.0000	0.0003	0.0012
Average for swd unbleached hi density storage	0.0488	0.0449	0.0007	0.0000	0.0010	0.0000	0.0000	0.0000	0.0000	0.0003	0.0014
TOTAL	**0.6341**	**0.5767**	**0.0202**	**0.0020**	**0.0109**	**0.0008**	**0.0020**	**0.0014**	**0.0001**	**0.0013**	**0.0033**
BLEACHING											
Bleached kraft with 50% substitution											
Mill F swd (D50,C+D, C+D)EODED	0.6800	0.5200	0.0006	0.0000	0.0011	0.0000	0.1200	0.0003	0.0008	0.0003	0.0220
Bleached kraft with 100% substitution											
Mill E swd DEDED (avg)	0.2700	0.2500	0.0030	0.0000	0.0010	0.0000	0.0110	0.0003	0.0001	0.0004	0.0019
Bleached kraft with oxygen delignification and 100% substitution											
Oxygen delignification	1.1492	1.1000	0.0430	0.0022	0.0040	0.0000	0.0001	0.0040	0.0001	0.0003	0.0001
Mill N swd OD(EP)DD	0.1800	0.1700	0.0036	0.0002	0.0001	0.0000	0.0020	0.0000	0.0001	0.0000	0.0001
TOTAL	**1.3292**	**1.2700**	**0.0466**	**0.0024**	**0.0041**	**0.0001**	**0.0021**	**0.0040**	**0.0001**	**0.0003**	**0.0002**
Bleached kraft with low effluent TCF											
Oxygen delignification	0.5732	0.5406	0.0274	0.0010	0.0042						
Bleach plant	0.1581	0.1350	0.0014	0.0204	0.0012						
TOTAL	**0.7313**	**0.6756**	**0.0288**	**0.0214**	**0.0054**						
CHEMICAL RECOVERY											
Mill M swd weak black liquor storage tank vent	0.0003	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Salt cake mix tank vents	0.0051	0.0045	0.0003	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Average for tall oil systems	0.0103	0.0093	0.0002	0.0000	0.0002	0.0000	0.0000	0.0000	0.0001	0.0001	0.0000
Causticizing	0.7450	0.7106	0.0124	0.0053	0.0025	0.0001	0.0020	0.0084	0.0006	0.0007	0.0013
Recovery boiler	0.4694	0.3611	0.0488	0.0121	0.0035	0.0003	0.0070	0.0016	0.0096	0.0018	0.0027
Chemical Recovery Total	**1.2301**	**1.0858**	**0.0617**	**0.0175**	**0.0063**	**0.0004**	**0.0091**	**0.0100**	**0.0102**	**0.0026**	**0.0040**

Note:
See Tables B-5 and B-6 and the associated notes for a complete compilation
of emission factors from pulp and paper mill sources from the NCASI 16 mill study.

Chlorofom emissions do not include fugitive emissions from wastewater handling and treatment systems.

Sources:
NCASI, "Volatile Organic Emissions from Pulp and Paper Mill Sources," *Technical Bulletins 675 - 684,* August- September 1994.

NCASI, "Compilation of 'Air Toxic' Emission Data from Boilers, Pulp Mills, and Bleach Plants," *Technical Bulletin 650,* September 1993, pp. 23, 24, 26-33, 34-37.

Table B-4. Volatile organic compound (VOC) and total reduced sulfur (TRS) air emissions from all sources at the mill

SOURCE	**acetone** (lb/ODTP)	**a-pinene** (lb/ODTP)	**b-pinene** (lb/ODTP)	**terpenes** (lb/ODTP)	**VOCs** C/ODTP)	**Methyl mercaptan** lb/ODTP	**Dimethyl sulfide** lb/ODTP	**Dimethyl disulfide** lb/ODTP	**TOTAL TRS** lb/ODTP
PULPING									
Brownstock screening to vent	0.0004	0.0000	0.0000	0.0014	0.0059	0.0001	0.0010	0.0003	0.0013
Average emissions from brownstock wash	0.0820	0.0064	0.0038	0.0000	0.6700	0.0000	0.0000	0.0000	0.0000
Swd decker hood & filtrate tank vents	0.1700	2.2000	0.5700	0.0000	1.4000	0.0000	0.0000	0.0000	0.0000
Average for swd unbleached hi density sto	0.0000	0.0000	0.0000	0.0000	0.0002	0.0000	0.0000	0.0000	0.0001
TOTAL	**0.2524**	**2.2064**	**0.5738**	**0.0014**	**2.0761**	**0.0001**	**0.0010**	**0.0003**	**0.0014**
BLEACHING									
Bleached kraft with 50% substitution									
Mill F swd (D50,C+D, C+D)EODED	0.0093	0.0000	0.0000	0.0440	0.3100	0.0070	0.0054	0.0068	0.0192
Bleached kraft with 100% substitution									
Mill E swd DEDED (avg)	0.0030	0.0008	0.0007	0.0000	0.0000	0.0145	0.0039	0.0058	0.0242
Bleached kraft with oxygen delignification and 100% substitution									
Oxygen delignification	0.0610	0.0310	0.0430	0.0230	0.6600	0.0006	0.0019	0.0012	0.0037
Mill N swd OD(EP)DD	0.0026	0.0026	0.0026	0.0026	0.0026	0.0026	0.0026	0.0026	0.0026
TOTAL	**0.0636**	**0.0336**	**0.0456**	**0.0256**	**0.6626**	**0.0032**	**0.0045**	**0.0038**	**0.0063**
Bleached kraft with low effluent TCF									
Oxygen delignification	0.0464								
Bleach plant	0.0043								
TOTAL	**0.0507**								
CHEMICAL RECOVERY									
Mill M swd weak black liquor storage tank	0.0001	0.0000	0.0000	0.0023	0.0008	0.0000	0.0000	0.0000	0.0001
Salt cake mix tank vents	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Average for tall oil systems	0.0062	0.0043	0.0210	0.0000	0.0000	0.0004	0.0640	0.0130	0.0774
Causticizing	0.0016	0.0000	0.0000	0.0889	0.5778	0.0004	0.0431	0.0010	0.0445
Recovery boiler	0.0037	0.0000	0.0000	0.1350	0.2630	0.0004	0.0088	0.0113	0.0205
Chemical Recovery Total	**0.0116**	**0.0043**	**0.0210**	**0.2262**	**0.8415**	**0.0013**	**0.1159**	**0.0253**	**0.1425**

Note:
See Tables B-5 and B-6 and the associated notes for a complete compilation of emission factors from pulp and paper mill sources from the NCASI 16 mill study.

EPA removed acetone from the list of VOCs in 1994 because of its low sensitivity to sunlight.
Total TRS does not include hydrogen sulfide. NCASI did not include this compound in its study.

Sources:
NCASI, "Volatile Organic Emissions from Pulp and Paper Mill Sources," *Technical Bulletins 675 - 684,* August- September 1994.

NCASI, "Compilation of 'Air Toxic' Emission Data from Boilers, Pulp Mills, and Bleach Plants," *Technical Bulletin 650,* September 1993, pp. 23, 24, 26-33, 34-37.

Table B-5. Hazardous air pollutant emissions from bleached kraft and TMP mills (1, 2, 3)

											1,2
Pulp mill location (4)	**Source (5)**	**Total HAPs (2)**	**Methanol**	**Chloroform (9)**	**Acetaldehyde**	**MEK (6)**	**Formaldehyde**	**n-hexane**	**MIBK (6)**	**Benzene**	**Styrene**
		(lb/ODTP)	(lb/ODTP)	(lb/ODTP)	(lb/ODTP)	(lb/ODTP)	(lb/ODTP)	(lb/ODTP)	(lb/ODTP)	(lb/ODTP)	(lb/ODTP)
Oxygen delignification	**I 85 (6)**	**1.1492**	**1.1000**	**0.0430**	**0.0022**	**0.0040**	**0.0000**	**0.0001**	**0.0040**	**0.0001**	**0.0003**
Emissions from Lime kilns, smelt dissolving tanks and misc. causticizing area vents											
Lime kilns	II/90 (7)	0.0397	0.0217	0.0040	0.0046	0.0004	0.0001	0.0007	0.0001	0.0003	0.0002
Smelt dissolving tanks	II/106 (4)	0.5597	0.5597	0.0010	0.0000	0.0014	0.0000	0.0009	0.0006	0.0002	0.0003
Slaker & Causticizing Vents	II/117 (3 + 2)	0.0397	0.0306	0.0064	0.0000	0.0003	0.0000	0.0001	0.0075	0.0000	0.0001
Lime mud washer	II/122 (1)	0.0321	0.0317	0.0000	0.0000	0.0001	0.0000	0.0001	0.0001	0.0000	0.0000
Lime Mud Precoat filter vents	II/129 (2)	0.0076	0.0067	0.0003	0.0001	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000
Precoat filter vacuum pump exhaust	II/132 (2)	0.0058	0.0055	0.0001	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000
Green Liquor clarifier vent	II/135 (1)	0.0428	0.0397	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000
Green liquor surge tank vent	II/137 (1)	0.0004	0.0003	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
White liquor clarifier	II/142 (1)	0.0058	0.0046	0.0000	0.0007	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000
White liquor filter	II/143 (1)	0.0113	0.0101	0.0006	0.0000	0.0001	0.0000	0.0001	0.0000	0.0000	0.0000
TOTALS	**0.0000**	**0.7450**	**0.7106**	**0.0124**	**0.0053**	**0.0025**	**0.0001**	**0.0020**	**0.0084**	**0.0006**	**0.0007**
Miscellaneous sources at kraft and TMP mills											
Mill G swd weak black liquor storage tank	III 106, B12 (1)	0.0127	0.0125	0.0001	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000
Mill G hwd weak black liquor storage	III 106, B13 (1)	0.0707	0.0687	0.0003	0.0000	0.0012	0.0001	0.0000	0.0000	0.0000	0.0000
Mill G combined int black liquor storage	III106, B14 (1)	0.0026	0.0021	0.0002	0.0000	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000
Mill G combined heavy black liquor storage tank	III 106, B15 (1)	0.0435	0.0302	0.0056	0.0001	0.0059	0.0000	0.0000	0.0000	0.0000	0.0001
Mill M swd weak black liquor storage tank vent	III 106, B25 (1)	0.0003	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ClO2 generators	t enough data to convert to lb/ODTP										
Swd decker hood & filtrate tank vents	III 120 (1)	0.0820	0.0670	0.0012	0.0000	0.0054	0.0000	0.0002	0.0001	0.0000	0.0003
Batch digester fill exhaust vents	III 130 (3)	0.0302	0.0258	0.0012	0.0008	0.0003	0.0001	0.0002	0.0000	0.0000	0.0002
Mill G swd unbleached hi density storage tank	III 136, B10	0.0951	0.0875	0.0013	0.0001	0.0020	0.0000	0.0001	0.0000	0.0000	0.0006
Mill O swd unbleached hi density storage tank	III 136, B34	0.0025	0.0023	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Average for swd unbleached hi density storage		0.0488	0.0449	0.0007	0.0000	0.0010	0.0000	0.0000	0.0000	0.0000	0.0003
Mill G hwd unbleached hi density storage tank	III 136, B11	0.4830	0.4590	0.0080	0.0004	0.0133	0.0002	0.0003	0.0002	0.0000	0.0004
Mill O hwd unbleached hi density storage tank	III 136, B32	0.0287	0.0271	0.0006	0.0000	0.0007	0.0000	0.0000	0.0001	0.0000	0.0001
Average for hwd unbleached hi density storage		0.2559	0.2431	0.0043	0.0002	0.0070	0.0001	0.0002	0.0001	0.0000	0.0002
Average for unbleached hi density storage tanks		0.1523	0.1440	0.0025	0.0001	0.0040	0.0001	0.0001	0.0001	0.0000	0.0003
Salt cake mix tank vents	III 143 (3)	0.0051	0.0045	0.0003	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000
Mill C tall oil recovery system	III 152	0.0050	0.0047	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.0001
Mill D tall oil recovery system	III 154	0.0040	0.0037	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000
Mill O tall oil system	III 156	0.0013	0.0010	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Average for tall oil systems		0.0103	0.0093	0.0002	0.0000	0.0002	0.0000	0.0000	0.0000	0.0001	0.0001
NCG thermal oxidizers	III 161 (3)	0.0110	0.0047	0.0012	0.0016	0.0001	0.0001	0.0002	0.0000	0.0004	0.0000
UNOX, activated sludge reactor	III170	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002	0.0000	0.0000	0.0000
TMP system	III 167	0.2840	0.1500	0.1300	0.0002	0.0041	0.0003	0.0006	0.0000	0.0003	0.0001

Table B-5. Hazardous air pollutant emissions from bleached kraft and TMP mills (cont'd)

Pulp mill location (4)	**Source (5)**	**Total HAPs (2)** (lb/ODTP)	**Methanol** (lb/ODTP)	**Chloroform (9)** (lb/ODTP)	**Acetaldehyde** (lb/ODTP)	**MEK (6)** (lb/ODTP)	**Formaldehyde** (lb/ODTP)	**n-hexane** (lb/ODTP)	**MIBK (6)** (lb/ODTP)	**Benzene** (lb/ODTP)	**Styrene** (lb/ODTP)	**1,2,4-trichloro benzene** (lb/ODTP)
Emissions from brownstock washing, screening and refining sources												
Brownstock screening to NCG collector	IV 77	0.6000	0.5900	0.0000	0.0001	0.0014	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000
Brownstock screening to vent	IV 80	0.0180	0.0160	0.0000	0.0006	0.0002	0.0000	0.0001	0.0000	0.0000	0.0000	0.0001
Mill A hwd VDW +twin roll press	IV 92	1.8000	1.7000	0.0390	0.0044	0.0035	0.0000	0.0007	0.0002	0.0000	0.0003	0.0002
Mill A swd VDW +twin roll press	IV 97	1.1000	1.1000	0.0290	0.0001	0.0090	0.0000	0.0150	0.0011	0.0000	0.0002	0.0013
Mill F horizontal belt washer filtrate tank	IV 100	0.0011	0.0009	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Mill G hwd diffusion washer	IV 103	0.1800	0.1700	0.0057	0.0001	0.0071	0.0001	0.0001	0.0001	0.0000	0.0003	0.0000
Mill G swd diffusion washer	IV 106	0.0480	0.0430	0.0018	0.0000	0.0017	0.0001	0.0000	0.0000	0.0000	0.0004	0.0000
Mill H cont. digester swd diffusion + 2VDW washers	IV 110	0.6200	0.5800	0.0190	0.0000	0.0063	0.0000	0.0013	0.0013	0.0001	0.0014	0.0001
Mill H batch digester + 4 VDW	IV 114	0.5600	0.5100	0.0220	0.0000	0.0050	0.0000	0.0014	0.0007	0.0003	0.0008	0.0003
Mill L hwd + 3 VDW in series	IV 118	0.7300	0.6900	0.0140	0.0051	0.0099	0.0003	0.0006	0.0006	0.0001	0.0033	0.0000
Mill L hwd diffusion washer + 1 VDW in series	IV 122	0.1700	0.1600	0.0083	0.0047	0.0007	0.0002	0.0005	0.0003	0.0001	0.0002	0.0001
Mill M 2 compaction baffle washers	IV 125	0.4500	0.2800	0.0760	0.0008	0.0074	0.0089	0.0003	0.0096	0.0002	0.0024	0.0055
Mill O hwd 2-stage pressure drum	IV 127	0.0900	0.0820	0.0024	0.0002	0.0011	0.0001	0.0001	0.0002	0.0000	0.0000	0.0000
Mill O swd 2-stage pressure drum	IV 130	0.0750	0.0690	0.0022	0.0002	0.0008	0.0001	0.0001	0.0002	0.0000	0.0000	0.0000
Average emissions from brownstock washers		0.4853	0.4487	0.0183	0.0013	0.0044	0.0008	0.0017	0.0012	0.0001	0.0008	0.0006
Emissions from kraft recovery furnaces and black liquor oxidation systems												
Recovery furnaces	VI 76 (10)	0.4694	0.3611	0.0488	0.0121	0.0035	0.0003	0.0070	0.0016	0.0096	0.0018	0.0027
Non-direct contact evaporator recovery furnaces	VI 79 (6)	0.3069	0.1986	0.0253	0.0148	0.0061	0.0003	0.0060	0.0061	0.0153	0.0017	0.0034
Direct contact evaporator recovery furnaces	VI 79 (4)	0.7403	0.5778	0.0776	0.0087	0.0085	0.0006	0.0087	0.0009	0.0012	0.0022	0.0014
NDCE recovery furnaces with wet bottom ESP	VI 81 (2)	0.4514	0.3792	0.0067	0.0060	0.0060	0.0003	0.0056	0.0008	0.0006	0.0015	0.0085
NDCE recovery furnaces with dry bottom ESP	VI 81 (4)	0.2528	0.1174	0.0361	0.0177	0.0063	0.0003	0.0061	0.0029	0.0235	0.0018	0.0010
NDCE furnaces with wet furnace ash handling	VI 83 (3)	0.2889	0.1463	0.0524	0.0181	0.0076	0.0003	0.0071	0.0034	0.0307	0.0023	0.0012
NDCE furnaces with dry furnace ash handling	VI 83 (1)	0.0813	0.0325	0.0067	0.0163	0.0023	0.0002	0.0032	0.0010	0.0002	0.0003	0.0005
Black liquor oxidation systems	VI 91 (2)	0.5778	0.4875	0.0740	0.0000	0.0135	0.0000	0.0007	0.0003	0.0004	0.0005	0.0004
Emissions from kraft mill bleach plants												
Mill A hwd O(DC)ED	V100	0.2800	0.2200	0.0098	0.0000	0.0007	0.0000	0.0410	0.0002	0.0001	0.0001	0.0005
Mill A swd O(DC)(EO)D(E+O)D	V 104	0.2300	0.1300	0.0100	0.0000	0.0011	0.0000	0.0820	0.0002	0.0001	0.0000	0.0003
Mill C hwd O(C85+D15)(EO)D	V 108	0.2200	0.1200	0.0026	0.0000	0.0012	0.0000	0.0890	0.0003	0.0004	0.0005	0.0001
Mill C swd O(C50+D50)(EO)D	V 112	0.2000	0.1300	0.0012	0.0000	0.0008	0.0000	0.0620	0.0002	0.0001	0.0006	0.0001
Mill E swd DEDED (avg)	V 122, 123	0.2700	0.2500	0.0030	0.0000	0.0010	0.0000	0.0110	0.0003	0.0001	0.0004	0.0019
Mill E hwd DEDED	V 127	0.1100	0.0830	0.0027	0.0000	0.0016	0.0000	0.0078	0.0032	0.0001	0.0012	0.0050
Mill F hwd (D,C50+D)(EOP)D	V 135	0.4600	0.1200	0.0009	0.0000	0.0003	0.0000	0.3300	0.0001	0.0001	0.0001	0.0070
Mill F swd (D50,C+D, C+D)EODED	V 140	0.6800	0.5200	0.0006	0.0000	0.0011	0.0000	0.1200	0.0003	0.0008	0.0003	0.0220
Mill J swd (D85, C+D)(EOP)D	V143	0.2100	0.1800	0.0024	0.0008	0.0005	0.0000	0.0230	0.0000	0.0000	0.0002	0.0000
Mill K hwd O(D50, C+D)(EO)DD (R3 generator)	V 147	0.1600	0.0420	0.0030	0.0021	0.0004	0.0000	0.1100	0.0000	0.0000	0.0000	0.0000
Mill L hwd O(D50,C+D)(EO)D	V 150	0.2700	0.0490	0.0017	0.0000	0.0005	0.0000	0.2200	0.0000	0.0000	0.0001	0.0001
Mill M hwd (D60, C+D)(E, O+P)D	V 153	0.0300	0.0110	0.0009	0.0004	0.0001	0.0000	0.0180	0.0000	0.0000	0.0000	0.0000
Mill M swd (D35, C+D)(E, O+P)DD	V 157	0.6800	0.3400	0.0310	0.0105	0.0014	0.0002	0.2700	0.0003	0.0002	0.0003	0.0007
Mill N swd OD(EP)DD	V 161	0.1800	0.1700	0.0036	0.0002	0.0001	0.0000	0.0020	0.0000	0.0001	0.0000	0.0001
Average hwd bleach plant	V 165 (6)	0.2400	0.0940	0.0027	0.0009	0.0005	0.0000	0.1300	0.0001	0.0001	0.0001	0.0013
Average swd bleach plant	V 166 (6)	0.3700	0.2600	0.0083	0.0055	0.0009	0.0001	0.0920	0.0002	0.0002	0.0003	0.0039

Notes: (1) This table includes emissions data for bleached kraft pulp mill and TMP mill locations. The NCASI study alsc emissions from pulp dryers and paper machines (Volume VII), sulfite mills (Volume VIII) and a Soda-based semichemical pulping process (Volume IX). NCASI tested these sources for 28 substances, 23 of which are classified as HAPs. The other five compounds include totally reduced sulfur compounds and VOCs including total hydrocarbons, acetone, alpha- and beta-pinene and terpenes. We selected the HAPs for this study that comprised at least one percent of the emissions of a pulp mill source.

(2) All emissions have been converted to pounds per oven-dried ton of pulp (lb/ODTP); emissions from caustisizi area are measured in lb/ton calcium oxide; emissions from heavy black liquor storage tanks and recovery furr in lb/ton of black liquor solids; emissions from tall oil recovery are measured in lb/ton of tall oil; emissions from batch digester vents are measured in lb/ton of moist chips.

CONVERSION FACTORS:
1 ton dry chips = 2 tons moist chips
1 ton air-dried pulp (ADTP) = 2 tons dry chips; 1 ton of air-dried pulp = 0.9 tons oven-dried pulp (ODTP)
1 ODTP = 4.44 tons of moist chips
Tons of black liquor solids per ADTP = 1.625; tons of black liquor solids per ODTP = 1.806
Tons of calcium oxide per ADTP = 0.275; tons of calcium oxide per ODTP = 0.306
Tons of tall oil per ADTP = 0.03; tons of tall oil per ODTP = 0.033

(3) All non-detectable samples and unconfirmed results are assumed to be 1/2 the detection limit.

(4) In some cases NCASI presents summary information from mills that use specific equipment combinations.

(5) Source refers to the references in the NCASI studies. Number in parentheses refers to the number of source to estimate the emissions.

(6) Chemical abbreviations: MEK = methyl ethyl ketone; MIBK = methyl isobutyl ketone

(7) We use these averages to estimate emissions from similar sources at different mills.

(8) We present the sources used to estimate the HAP air emissions in Table 1 in boldface type.

(9) Chloroform emissions do not include fugitive emissions from wastewater handling and treatment.

Source: NCASI, Technical Bulletins 674 - 680, August - November 1994.

Table B-6. Volatile organic compounds (VOC) and total reduced sulfur (TRS) from pulp and paper mills.

Process	Source	Acetone (9) (lb/ODTP)	a-pinene (lb/ODTP)	b-pinene (lb/ODTP)	Terpenes (lb/ODTP)	VOCs lb C/ODTP	Methyl mercaptan lb/ODTP	Dimethyl sulfide lb/ODTP	Dimethyl disulfide lb/ODTP	TOTAL TRS (9) lb/ODTP
Emissions from Lime kilns, smelt dissolving tanks a	**I 85**	0.0610	0.0310	0.0430	0.0230	0.6600	0.0006	0.0019	0.0012	0.0037
Emissions from Lime kilns, smelt dissolving tanks and misc. cau		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Lime kilns	II/90	0.0024	0.0000	0.0000	0.0119	0.0189	0.0020	0.0024	0.0031	0.0075
Smelt dissolving tanks	II/106	0.0060	0.0007	0.0235	0.0130	0.0000	0.0010	0.0017	0.0025	0.0053
Slaker & Causticizing Vents	II/117	0.0029	0.0000	0.0000	0.0021	0.0113	0.0001	0.0002	0.0001	0.0004
Lime mud washer	II/122	0.0003	0.0000	0.0000	0.0024	0.0275	0.0002	0.0004	0.0001	0.0007
Lime Mud Precoat filter vents	II/129	0.0002	0.0000	0.0000	0.0008	0.0037	0.0001	0.0002	0.0002	0.0004
Precoat filter vacuum pump exhaust	II/132	0.0003	0.0000	0.0000	0.0015	0.0055	0.0000	0.0002	0.0001	0.0003
Green Liquor clarifier vent	II/135	0.0000	0.0000	0.0000	0.0019	0.0202	0.0001	0.0000	0.0001	0.0002
Green liquor surge tank vent	II/137	0.0000	0.0000	0.0000	0.0004	0.0004	0.0000	0.0000	0.0000	0.0000
White liquor clarifier	II/142	0.0002	0.0000	0.0000	0.0010	0.0017	0.0001	0.0002	0.0003	0.0006
White liquor filter	II/143	0.0004	0.0000	0.0000	0.0043	0.0023	0.0002	0.0002	0.0003	0.0006
TOTALS		**0.0126**	**0.0007**	**0.0235**	**0.0394**	**0.0915**	**0.0039**	**0.0055**	**0.0066**	**0.0160**
Miscellaneous sources at kraft and TMP mills										
Mill G swd weak black liquor storage tank	III 106, B12	0.0003	0.0000	0.0000	0.0025	0.0104	0.0000	0.0007	0.0002	0.0009
Mill G hwd weak black liquor storage	III 106, B13	0.0043	0.0000	0.0000	0.1010	0.0859	0.0002	0.0130	0.0038	0.0170
Mill G combined int black liquor storage	III 106, B14	0.0004	0.0000	0.0000	0.0002	0.0016	0.0001	0.0010	0.0005	0.0016
Mill G combined heavy black liquor storage tank	III 106, B15	0.0076	0.0000	0.0000	0.0019	0.0164	0.0003	0.0226	0.0043	0.0271
Mill M swd weak black liquor storage tank vent	III 106, B25	0.0001	0.0000	0.0000	0.0023	0.0008	0.0000	0.0000	0.0000	0.0001
ClO2 generators	III 113	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Swd decker hood & filtrate tank vents	III 120	0.0062	0.0043	0.0210	0.0000	0.0000	0.0004	0.0640	0.0130	0.0774
Batch digester fill exhaust vents	III 130	0.0016	0.0000	0.0000	0.0889	0.5778	0.0004	0.0431	0.0010	0.0445
Mill G swd unbleached hi density storage tank	III 136, B10	0.0037	0.0000	0.0000	0.1350	0.2630	0.0004	0.0088	0.0113	0.0205
Mill O swd unbleached hi density storage tank	III 136, B34	0.0001	0.0000	0.0000	0.0005	0.0070	0.0000	0.0000	0.0000	0.0001
Average for swd unbleached hi density storage		**0.0019**	**0.0000**	**0.0000**	**0.0677**	**0.1350**	**0.0002**	**0.0044**	**0.0057**	**0.0103**
Mill G hwd unbleached hi density storage tank	III 136, B11	0.0237	0.0000	0.0000	0.0716	0.4260	0.0025	0.0479	0.0346	0.0850
Mill O hwd unbleached hi density storage tank	III 136, B32	0.0013	0.0000	0.0000	0.0873	0.0962	0.0000	0.0075	0.0122	0.0197
Average for hwd unbleached hi density storage		**0.0125**	**0.0000**	**0.0000**	**0.0795**	**0.2611**	**0.0012**	**0.0277**	**0.0234**	**0.0523**
Average for unbleached hi density storage tanks		**0.0072**	**0.0000**	**0.0000**	**0.0736**	**0.1980**	**0.0007**	**0.0160**	**0.0145**	**0.0313**
Salt cake mix tank vents	III 143	0.0003	0.0000	0.0000	0.0002	0.0054	0.0002	0.0047	0.0022	0.0070
Mill C tall oil recovery system	III 152	0.0009	0.0000	0.1367	0.0000	1.7000	0.0000	0.0000	0.0000	0.0000
Mill D tall oil recovery system	III 154	0.0050	0.0000	0.0000	0.0000	0.0967	0.0002	0.0000	0.0000	0.0002
Mill O tall oil system	III 156	0.0005	0.0000	0.0000	0.0053	0.0037	0.0001	0.0000	0.0000	0.0002
Average for tall oil systems		**0.0021**	**0.0000**	**0.0456**	**0.0018**	**0.6001**	**0.0001**	**0.0000**	**0.0000**	**0.0001**
NCG thermal oxidizers	III 161	0.0008	0.0000	0.0001	0.0250	0.0180	0.0005	0.0007	0.0010	0.0022
UNOX, activated sludge reactor	III170	0.0000	0.0000	0.0000	0.0005	0.0190	0.0000	0.0000	0.0000	0.0000
TMP system	III 167	**0.0680**	**0.0000**	**0.0000**	**0.6300**	**0.3100**	**0.0010**	**0.0013**	**0.0020**	**0.0043**

Table B-6. Volatile organic compounds (VOC) and total reduced sulfur (TRS) from pulp and paper mills. (Cont'd)

Process	**Source**	**Acetone (9)** (lb/ODTP)	**a-pinene** (lb/ODTP)	**b-pinene** (lb/ODTP)	**Terpenes** (lb/ODTP)	**VOCs** lb C/ODTP	**Methyl mercaptan** lb/ODTP	**Dimethyl sulfide** lb/ODTP	**Dimethyl disulfide** lb/ODTP	**TOTAL TRS (9)** lb/ODTP
Emissions from brownstock washing, screening and refining sources										
Brownstock screening to NCG collector	IV 77	0.0190	0.0005	0.0002	0.0000	0.1600	0.0000	0.0000	0.0000	0.0000
Brownstock screening to vent	IV 80	0.0004	0.0000	0.0000	0.0014	0.0059	0.0001	0.0010	0.0003	0.0013
Mill A hwd VDW +twin roll press	IV 92	0.0820	0.0064	0.0038	0.0000	0.6700	0.0000	0.0000	0.0000	0.0000
Mill A swd VDW +twin roll press	IV 97	0.1700	2.2000	0.5700	0.0000	1.4000	0.0000	0.0000	0.0000	0.0000
Mill F horizontal belt washer filtrate tank	IV 100	0.0000	0.0000	0.0000	0.0000	0.0002	0.0000	0.0000	0.0000	0.0001
Mill G hwd diffusion washer	IV 103	0.0120	0.0000	0.0000	0.0430	0.1900	0.0014	0.0510	0.0300	0.0824
Mill G swd diffusion washer	IV 106	0.0038	0.0000	0.0000	0.0007	0.3000	0.0004	0.0160	0.0180	0.0344
Mill H cont. digester swd diffusion + 2VDW washers	IV 110	0.0690	0.0000	0.0000	6.6000	2.2000	0.0017	0.0380	0.0054	0.0451
Mill H batch digester + 4 VDW	IV 114	0.0320	0.0000	0.0000	5.0000	0.2300	0.0041	0.0110	0.0130	0.0281
Mill L hwd + 3 VDW in series	IV 118	0.0250	0.0000	0.0000	0.0120	0.5700	0.0067	0.7200	0.0480	0.7747
Mill L hwd diffusion washer + 1 VDW in series	IV 122	0.0082	0.0000	0.0000	0.0051	0.1300	0.0015	0.1100	0.0058	0.1173
Mill M 2 compaction baffle washers	IV 125	0.1100	0.0000	0.0000	0.0000	5.6000	0.0180	1.2000	0.0780	1.2960
Mill O hwd 2-stage pressure drum	IV 127	0.0074	0.0000	0.0000	0.2800	0.1400	0.0002	0.0130	0.0019	0.0151
Mill O swd 2-stage pressure drum	IV 130	0.0054	0.0000	0.0000	0.3300	0.2200	0.0002	0.0110	0.0021	0.0133
Average emissions from brownstock washers		**0.0437**	**0.1839**	**0.0478**	**1.0226**	**0.9709**	**0.0034**	**0.2170**	**0.0202**	**0.2406**
Emissions from kraft recovery furnaces and black liquor oxidation systems										
Recovery furnaces	VI 76	0.0253	0.0036	0.0083	0.0069	0.2708	0.0144	0.0181	0.0280	0.0605
Non-direct contact evaporator recovery furnaces	VI 79	0.0107	0.0036	0.0083	0.0650	0.3250	0.0126	0.0153	0.0235	0.0515
Direct contact evaporator recovery furnaces	VI 79	0.0469	0.0000	0.0000	0.0704	0.1556	0.0172	0.0226	0.0343	0.0740
NDCE recovery furnaces with wet bottom ESP	VI 81	0.0199	0.0000	0.0000	0.1661	0.1733	0.0117	0.0153	0.0235	0.0506
NDCE recovery furnaces with dry bottom ESP	VI 81	0.0063	0.0036	0.0083	0.0325	0.4333	0.0126	0.0163	0.0244	0.0533
NDCE furnaces with wet furnace ash handling	VI 83	0.0072	0.0036	0.0083	0.0451	0.6319	0.0153	0.0199	0.0298	0.0650
NDCE furnaces with dry furnace ash handling	VI 83	0.0038	0.0000	0.0000	0.0081	0.0034	0.0068	0.0087	0.0135	0.0290
Black liquor oxidation systems	**VI 91**	**0.0668**	**0.0000**	**0.0000**	**0.3250**	**0.3611**	**0.0101**	**0.0087**	**0.0163**	**0.0350**
Emissions from kraft mill bleach plants										
Mill A hwd O(DC)ED	V100	0.0059	0.0007	0.0002	0.0000	0.0880	0.0000	0.0000	0.0000	0.0000
Mill A swd O(DC)(EO)D(E+O)D	V 104	0.0060	0.0018	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Mill C hwd O(C85+D15)(EO)D	V 108	0.0064	0.0020	0.0100	0.0000	0.0220	0.0000	0.0000	0.0000	0.0000
Mill C swd O(C50+D50)(EO)D	V 112	0.0120	0.0038	0.0057	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Mill E swd DEDED (avg)	V 122, 123	0.0030	0.0008	0.0007	0.0000	0.0000	0.0145	0.0039	0.0058	0.0242
Mill E hwd DEDED	V 127	0.0010	0.0012	0.0002	0.0000	0.0000	0.0027	0.0034	0.0050	0.0111
Mill F hwd (D,C50+D)(EOP)D	V 135	0.0035	0.0000	0.0000	0.0060	0.0500	0.0028	0.0030	0.0029	0.0087
Mill F swd (D50,C+D, C+D)EODED	V 140	0.0093	0.0000	0.0000	0.0440	0.3100	0.0070	0.0054	0.0068	0.0192
Mill J swd (D85, C+D)(EOP)D	V143	0.0037	0.0000	0.0000	0.0034	0.0500	0.0003	0.0005	0.0007	0.0015
Mill K hwd O(D50, C+D)(EO)DD (R3 generator)	V 147	0.0031	0.0000	0.0000	0.0088	0.2000	0.0005	0.0007	0.0010	0.0022
Mill L hwd O(D50,C+D)(EO)D	V 150	0.0013	0.0000	0.0000	0.0028	0.0360	0.0007	0.0009	0.0014	0.0030
Mill M hwd (D60, C+D)(E, O+P)D	V 153	0.0006	0.0000	0.0000	0.0005	0.0100	0.0002	0.0002	0.0004	0.0008
Mill M swd (D35, C+D)(E, O+P)DD	V 157	0.0120	0.0000	0.0000	0.0250	0.1200	0.0044	0.0044	0.0085	0.0173
Mill N swd OD(EP)DD	V 161	0.0026	0.0000	0.0000	0.0028	0.0250	0.0065	0.0010	0.0015	0.0090
Average hwd bleach plant	**V 165**	**0.0035**	**0.0013**	**0.0052**	**0.0045**	**0.0680**	**0.0010**	**0.0012**	**0.0014**	**0.0036**
Average swd bleach plant	**V 166**	**0.0073**	**0.0036**	**0.0240**	**0.0039**	**0.1500**	**0.0060**	**0.0024**	**0.0065**	**0.0149**

Table B-6. Volatile organic compounds (VOC) and total reduced sulfur (TRS) from pulp and paper mills. (Cont'd)

	Source (lb/ODTP)	**Acetone (9)** (lb/ODTP)	**a-pinene** (lb/ODTP)	**b-pinene** (lb/ODTP)	**Terpenes** lb C/ODTP	**VOCs** lb/ODTP	**methyl mercaptan** lb/ODTP	**dimethyl sulfide** lb/ODTP	**dimethyl disulfide** lb/ODTP	**TOTAL TRS (9)**
Emissions from paper machines and pulp dryers (lb/air dried ton of finished product)										
Mill G linerboard paper machine	VII54	0.0530	0.0000	0.0000	0.2500	0.6000	0.0110	0.0140	0.0200	0.0450
Mill H linerboard machine	VII 60	0.0340	0.0000	0.0000	1.5000	0.4200	0.0360	0.0465	0.0700	0.1525
Mill K paper machine 50%bleached hwd/swd	VII 66	0.0300	0.0000	0.0000	0.0880	0.0380	0.0130	0.0170	0.0255	0.0555
Mill K coater (nonvolatile coating)	VII 67	0.0015	0.0000	0.0000	0.0073	0.0170	0.0041	0.0055	0.0080	0.0176
Mill N pulp dryer	VII 73	0.0120	0.0000	0.0000	0.0370	0.1000	0.0099	0.0080	0.0125	0.0304
Mill Q corrugating medium w/33% recycled content	VII 79	0.0250	0.0000	0.0000	0.0360	0.2500	0.0255	0.0325	0.0500	0.1080

Notes: (1) This table includes emissions data for bleached kraft pulp mill and TMP mill locations. The NCASI study also evaluated emissions from pulp dryers and paper machines (Volume VII), sulfite mills (Volume VIII) and a Soda-based semichemical pulping process (Volume IX). NCASI tested these sources for 28 substances, 23 of which are classified as HAPs. The other five compounds include totally reduced sulfur compounds and VOCs including total hydrocarbons, acetone, alpha- and beta-pinene and terpenes. We selected the HAPs for this study that comprised at least one percent of the emissions of a pulp mill source.

(2) All emissions have been converted to pounds per oven-dried ton of pulp (lb/ODTP); emissions from caustisizing area are measured in lb/ton calcium oxide; emissions from heavy black liquor storage tanks and recovery furnaces are measured in lb/ton of black liquor solids; emissions from tall oil recovery are measured in lb/ton of tall oil; emissions from batch digester vents are measured in lb/ton of moist chips.

CONVERSION FACTORS:
1 ton dry chips = 2 tons moist chips
1 ton air-dried pulp (ADTP) = 2 tons dry chips; 1 ton of air-dried pulp = 0.9 tons oven-dried pulp (ODTP)
1 ODTP = 4.44 tons of moist chips
Tons of black liquor solids per ADTP = 1.625; tons of black liquor solids per ODTP = 1.806
Tons of calcium oxide per ADTP = 0.275; tons of calcium oxide per ODTP = 0.306
Tons of tall oil per ADTP = 0.03; tons of tall oil per ODTP = 0.33

(3) All non-detectable samples and unconfirmed results are assumed to be 1/2 the detection limit.

(4) In some cases NCASI presents summary information from mills that use specific equipment combinations.

(5) Source refers to the references in the NCASI studies. Number in parentheses refers to the number of sources used to estimate the emissions.

(6) Chemical abbreviations: MEK = methyl ethyl ketone; MIBK = methyl isobutyl ketone

(7) We use these averages to estimate emissions from similar sources at different mills.

(8) We present the sources used to estimate the HAP air emissions in Table 1 in boldface type.

(9) EPA removed acetone from the list of VOCs in 1994 because of its low sensitivity to sunlight.
Total TRS does not include hydrogen sulfide. NCASI did not include this compound in its study.

Source: NCASI, Technical Bulletins 674 - 680, August - November 1994.

Table B-7. TCDD and TCDF loading in the final effluent of softwood bleached kraft mills with traditional and enhanced ECF bleaching

		Mill 1 [1]					Mill 2 [2]					Mill 3 [1]
		Traditional ECF					Traditional ECF					Traditional E
		TCDD [a]		TCDF [b]			TCDD [a]		TCDF [b]			TCDD [a]
Number		(ppq)		(ppq)	Number		(ppq)		(ppq)	Number		(ppq)
1	ND	0.1	ND	1.2	1	ND	2.7		**17**	1	ND	2.5
2	ND	0.8		**13.0**	2	ND	3.2		**9**	2	ND	3
3	ND	3.7		**4.9**	3	ND	1.3	ND	3.3	3	ND	4.2
4	ND	3.7		**6.1**	4	ND	1.3	ND	1.7	4	ND	3.1
5	ND	2.5		**12.0**	5	ND	2.8	ND	3.5	5	ND	1.9
6	ND	0.8		**9.1**	6	ND	1.9		**3.2**			
7	ND	2.4		**4.6**	7	ND	3.8	ND	2.3			
8	ND	1.6		**8.0**	8	ND	1.4	ND	1.9			
9	ND	2.0		**13.0**	9	ND	2.7	ND	3			
10	ND	1.6		**5.9**								
11	ND	3.1		**22.0**								
12	ND	1.8		**21.0**								
13	ND	1.6		**20.0**								
14	ND	2.2	ND	1.9								
15	ND	3.6	ND	5.0								
16	ND	1.1		**5.9**								
dF [c]				15					8			
Mean				9.35					4.12			
St. Dev				6.91					5.46			

Notes: [a] Samples belowthe detection limit have ND followed by the reported limit of detection. To calculate the mean, we have counted these "non-detects" at half the detection limit.
[b] Numbers in boldface indicatetaht TCDF was detected in the effluent sample.
[c] dF refers to degrees of freedom.

Sources: [1] Alberta Department of Environmental Protection
[2] Alan Stincfield and Michael Woods, "Reduction chlorinated organic compounds from bleached kraft mills through first stage substitution of chlorine dioxide for chlorine," *Tappi Journal,* **78(6)**: 120 (1995).

Comparisons of traditional ECF and enhanced ECF

Comparison 1: Mill 1 and Mill 3	
Difference in means	6.40
dF(Mill 1)	4
dF(Mill 3)	15
pooled st. dev.	6.21
std. error	3.49
t	**1.83**
p(t <0.5, dF = 19)	2.09

Do not reject Ho at p=0.5 [1]

Comparison 1: Mill 1 and Mill 3	
Difference in means	1.17
dF(Mill 1)	4.00
dF(Mill 3)	8.00
pooled st. dev.	4.61
std. error	2.83
t	**0.41**
p(t <0.5, dF = 19)	2.09

Do not reject Ho at p=0.5 [1]

[1] We cannot reject the null hypothesis that the means are NOT different 95% of the time.

IX. ENDNOTES

[1] American Forest & Paper Association, *Paper, Paperboard, Pulp Capacity and Fiber Consumption 1992 - 1996 -- 34th Annual Survey*, (Washington, DC: American Forest & Paper Association, 1993), 10; Food and Agriculture Organization of the United Nations, *Pulp and Paper Capacities -- Survey 1992 - 1997* (Rome: FAO, 1993), 160.

[2] The only exception is Louisiana-Pacific's mill in Samoa, CA. Effluent from this mill undergoes primary treatment and is then discharged in the Pacific Ocean several miles off-shore.

[3] Pertti Laine, "Environmental Protection by the Finnish Forest Industry," *What is Determining International Competitiveness in the Global Pulp and Paper Industry?*- Proceedings of the CINTRAFOR Third International Symposium (Seattle, WA: University of Washington, College of Forest Resources, September 13-14, 1994), 77-99.

[4] Gary A. Smook, *Handbook For Pulp and Paper Technologists, 2nd. Ed*. (Vancouver: Angus Wilde Publications, 1992), 82 - 83.

[5] D. Lachenal and N.B Nguyen -Thi, "TCF Bleaching - Which sequence to choose?" *Proceedings of the 1993 Pulping Conference* (Atlanta: TAPPI Press, 1993), 799 - 804.

[6] Researchers are exploring uses for enzymes throughout the pulp mill, but uses that reduce the quantity of bleaching chemicals required to produce high brightness pulps have received the most attention. [Roger L. Grant, "Enzymes - A New Tool for Pulping and Bleaching", *Market Pulp 9: Meeting the Challenge of the '90s*, Brussels, Belgium, May 9 - 10, 1994.] German scientists have developed a novel enzyme system that uses an enzyme to activate a chemical that then reacts with the lignin in the pulp. Based on laboratory tests, they claim to be able to remove 67% of the remaining lignin from an oxygen delignified pulp while maintaining pulp strength. [H. P. Call and I. Mücke, "State of the Art of Enzyme Bleaching and Disclosure of a Breakthrough Process," *Proceedings of the 1994 International Non-Chlorine Bleaching Conference* (San Francisco: Miller Freeman, Inc., 1994). *1994 International Non-Chlorine Bleaching Conference*, hereafter.] Process development continues, but other research laboratories have difficulty reproducing the results. [Norman Liebergott, consultant, DuPont Canada, personal communication, March 7, 1995.]

Peracids are formed by reacting a strong acid with hydrogen peroxide. Peracetic acid, a mixture of hydrogen peroxide and highly purified acetic acid, and Caro's acid, a mixture of hydrogen peroxide and concentrated sulfuric acid, have been developed to improve the brightness of TCF pulps. In the lab study, scientists increased the brightness of a hardwood kraft pulp from 86 to 90 ISO by substituting Caro's acid for a hydrogen peroxide stage in a three stage hydrogen peroxide TCF bleaching sequence. [N. A. Troughton, F. Desprez, J. Devenyns, "Peracids: The Pathway to High Brightness TCF Pulps," *1994 International Non-Chlorine Bleaching Conference*.] Mills are currently evaluating this technology.

[7] The abbreviation "ED" for extended delignification is not a standard abbreviation developed by the Technical Association of the Pulp and Paper Industry (TAPPI).

[8] John Gray and Peter Axegard, "Choice of ClO_2 System Can Minimize Costs, Satisfy Mill Byproduct Needs," in Ken Patrick, ed., *Bleaching Technology for Chemical and Mechanical Pulps*, (San Francisco: Miller Freeman, Inc., 1991), 50.

[9] 20% of the chlorine dioxide used in the first bleaching stage is converted into chlorate in a medium consistency bleaching tower and does not react with the lignin. [Douglas Reeve, Kathleen Weishar and Li Li, "Process Modifications to Decrease Organochlorine Formation During Chlorine Dioxide

Delignification," *J. Pulp and Paper Sci,* 21(6): J197-J202.] At low pH, chlorine dioxide oxidizes the pulp and eventually is transformed into hypochlorous acid. [W. Howard Rapson and Gene Strumila, "Chlorine Dioxide Bleaching," in Rudy Singh (ed.), *The Bleaching of Pulp*, Third Edition, Revised (Atlanta: TAPPI Press, 1991), 135-136.] At low pH, about half of the hypochlorous acid is converted into elemental chlorine. [Carlton Dence and Göran Annergren, "Chlorination," in Rudy Singh (ed.), *The Bleaching of Pulp*, Third Edition, Revised (Atlanta: TAPPI Press, 1991), 32.]

[10] Y. Ni, G.J. Kubes, and A.R.P. Van Heiningen, "Chlorination Kinetics of Kraft Pulp," *J. Pulp and Paper Sci.,* **21(1)**: J32 (1995). Gierer points out that the reactions of hypochlorous acid and aromatic rings are the same as those of elemental chlorine. [J. Gierer, "Chemistry of Delignification Part 2: Reactions of lignins during bleaching," *Wood Sci. Technol*., **20**: 2-4 (1986). Elemental chlorine and hypochlorous acid do react differently with other parts of the lignin molecule to produce less stable chlorinated organic compounds. [Ibid, p. 7].

[11] G. Maples *et al.,* "BFR: A New Process Toward Bleach Plant Closure," *Papers presented at the 1994 International Pulp Bleaching Conference*, Vancouver, BC, June 13-16, 1994, 253 - 262. (*1994 International Pulp Bleaching Conference* hereafter) BFR™ is a licensed trademark of Champion International.

[12] Kirk A. Girard and Anton F. Jaegel, "TCF Bleaching at Louisiana-Pacific Corp.'s Samoa Pulp Mill, Calif.," *Proceedings of the 1995 International Non-Chlorine Bleaching Conference* (San Francisco: Miller Freeman Inc., March 1995). (*1995 International Non-Chlorine Bleaching Conference* hereafter.)

[13] Roland Lövblad, manager, Environmental Services, Södra Cell AB, Paper Task Force Expert Panel, September 21, 1994.

[14] At its Husum mill, MoDo uses the bleach plant filtrates from the *hardwood* fiber line as shower water in the oxygen delignification system of its *softwood* fiber line. The filtrates from the hardwood line are sent to the recovery boiler; thus, the hardwood line discharges no bleach plant filtrates. The softwood bleach plant runs without any effluent recirculation. [Kirk Girard, environmental manager, Louisiana-Pacific, technical meeting with environmental groups, Washington, DC, 7 November 1995.]

[15] Tim Evans, et. al., "Applying Proven TEF Technology to ECF Kraft Mill Closure," *1994 International Non-Chlorine Bleaching Conference*.

[16] Dag Strömqvist, "New Technology Development for the Closed Cycle Bleach Plant," *Second Global Conference on Paper & the Environment*, Frankfurt, 24 - 26 April, 1994.

[17] J. Drew Ricketts, "Considerations for the closed-cycle mill," *Tappi Journal*, **77(11)**: 45 (1994).

[18] Gerard Closset, vice president, technology development, Champion International, letter to Harry Capell, 11 July 1995, p. 4.

[19] D. R. Ester, "Reduction of Bleach Plant Deposits Yields Better Pulp, Less Downtime," *Pulp & Paper*, 68(9):135 (1994).

[20] Ibid.

[21] Mirjam Schoonenboom and Kees Olie, "Formation of PCDDs and PCDFs from Anthracene and Chloroanthracene in a Model Fly Ash System," *Environ. Sci. Technol*. **29(8):** 2005 - 2009 (1995); Ruud Addink and Kees Olie, "Mechanisms of formation and destruction of polychlorinated dibenzo-p-dioxins and dibenzofurans in heterogeneous systems," *Environ. Sci. Technol.*, **29(6)**: 1425-1435 (1995).

[22] Kirk Girard, environmental manager, Louisiana-Pacific, Samoa, CA, technical presentation to the environmental community, Washington, DC, 7 November 1995.

[23] U.S. EPA, Office of Water, *Development Document for Proposed Effluent Limitations Guidelines and Standards for the Pulp, Paper and Paperboard Point Source Category* (Washington, DC: EPA-821-R-93-019, October 1993), p. 4-20. (*Development Document* hereafter)

[24] U.S. EPA (Office of Pollution Prevention and Toxics), *Pollution Prevention Technologies for the Bleached Kraft Segment of the U.S. Pulp and Paper Industry* (Washington, DC: EPA/600/R-93/110, 1993), 2-12. (*Pollution Prevention Technologies* hereafter)

[25] Thomas McDonough, "Recent advances in bleached chemical pulp manufacturing technology Part 1," *Tappi Journal*, **78(3)**: 55 (1995).

[26] *Trends in World Bleached Chemical Pulp Production: 1990-1995* (Washington, DC: Alliance for Environmental Technology, 1995), 4.

[27] Kelly H. Ferguson, "Union Camp Begins Ozone Era with New Kraft Bleaching Line at Franklin, VA," *Pulp & Paper*, **66(11)**: 42 (1992).

[28] Thomas Govers, "Non-Chlorine Bleaching Technologies in the 21st Century," panel discussion, 1995 International Non-Chlorine Bleaching Conference, Amelia Island, FL, 9 March 1995.

[29] Kirk A. Girard and Anton F. Jaegel, "TCF Bleaching at Louisiana-Pacific Corp.'s Samoa Pulp Mill, Calif."

[30] Roland Lövblad, manager, Environmental Services, Södra Cell AB, Värö, Sweden, personal communication, June 8, 1995.

[31] Carl-Johan Alfthan, "Pollution Reduction - Targets, Achievements and the Public," *Proceedings of the Third Global Conference on Paper and the Environment*, London, England, 26-28 March 1995, 111-115.

[32] Panel on Pulp Quality and Economics of ECF vs. TCF Bleaching, 1995 International Non-Chlorine Bleaching Conference, Amelia Island, FL, 7 March 1995.

[33] U.S. EPA, *Regulatory Impact Assessment of Proposed Effluent Guidelines and NESHAP for the Pulp, Paper and Paperboard Industry*, (Washington: Office of Water, EPA-821-R93-020, November 1993), 7-25 - 7-26. (*Regulatory Impact Assessment,* hereafter).

[34] Kirsten Vice, Roy Sieber and Betsy Bicknell, "Costs of Upgrading Bleach Plants to Minimize COD discharges," *1995 International Non-Chlorine Bleaching Conference*, 21; Rolf Helander, Stora Billerud, Panel on Mill Experience with Ozone Bleaching Worldwide, 1994 International Non-Chlorine Bleaching Conference, Amelia Island, FL, March 1994.

[35] Wells Nutt, president, Union Camp Technologies Inc., letter to Harry Capell, Johnson & Johnson, 12 July 1995.

[36] Gerard Closset, letter to Harry Capell, 11 July 1995. Elaahi and Lowitt report the energy consumed to evaporate black liquor to range from 2.0 - 4.0 million Btu's per oven-dried ton of pulp. [Source: A. Elaahi and H.E. Lowitt, *The U.S. Pulp & Paper Industry and Energy Perspective*, report for the Department of Energy, DE88-008615 by Energetics Inc., April 1988, 4-3.]

[37] Torolf Laxén and Kaj Henricson, “Energy Efficiency in ECF and TCF Bleaching,” *1994 International Pulp Bleaching Conference*, 241- 245.

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[39] Roland Lövblad, manager, Environmental Services, Södra Cell, Paper Task Force Expert Panel, September 21, 1994.

[40] Wells Nutt, president, Union Camp Technologies Inc., letter to Lauren Blum, Environmental Defense Fund, 27 September 1994.

[41] Wells Nutt, letter to Harry Capell, 5.

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[43] Jean Renard, Paper Task Force presentation, Newark, NJ, 1 September 1994.

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[45] NCASI, “Generation and Emissions of Selected HAPs at a TCF Mill,” presented at the NCASI Southern Regional Meeting, August 1995.

[46] G. Maples et al*., 1994 International Pulp Bleaching Conference*, 261.

[47] *Federal Register*, **58**, December 17, 1993, 66081.

[48] U.S. EPA, *Regulatory Impact Assessment*, 7-7 - 7-8.

[49] NCASI, “Volatile Organic Emissions from Pulp and Paper Mill Sources Part IV - Brownstock Washing, Screening and Refining Sources,” *Technical Report No. 678*, September 1994, 110.

[50] NCASI, “Volatile Organic Emissions from Pulp and Paper Mill Sources Part I - Oxygen Delignification Systems,” *Technical Report No. 675*, August 1994, 85.

[51] NCASI, “Volatile Organic Emissions from Pulp and Paper Mill Sources Part VI - Recovery Furnaces and Black Liquor Oxidation Systems,” *Technical Report No. 680*, October 1994, 76.

[52] In his review of a draft of White Paper No. 5, Harry Hintz of Westvaco noted that the chloroform concentrations in the filtrates of traditional ECF bleach plants were lower than those from enhanced ECF bleach plants. The NCASI 16 mill study does not measure the chloroform concentration in the filtrates of the mill with an enhanced ECF process. As a result, we cannot make a direct comparison of the total chloroform concentration generated by these processes. A NCASI study of the effluents of six ECF bleached kraft pulp mills in Canada does measure the chloroform concentration in the bleach plant filtrates of mills. This study shows mean chloroform concentrations of 0.52 and 1.86 grams chloroform per metric ton of softwood bleached kraft pulp, respectively, in the bleach plant filtrates of mills with traditional ECF processes and enhanced ECF processes. [NCASI, “Characterization of Effluent Quality at Seven Canadian Kraft Mills Operating Complete Substitution Bleach Plants,” *Special Report No. 95-09*, July 1995, 10.] The total chloroform concentration of 2.86 grams per air-dried metric ton of softwood bleached kraft pulp generated by the mill with the enhanced ECF process is lower than that of the mill with a traditional ECF process at 6.02 grams of chloroform per air-dried metric ton of softwood bleached kraft pulp.

[53] Robert J. Crawford *et al.,* "Chloroform generation at bleach plants with high chlorine dioxide

substitution or oxygen delignification," *Tappi Journal*, **74(4)**: 163 (1991).

[54] NCASI, "Volatile Organic Emissions from Pulp and Paper Mill Sources: Part I - Oxygen Delignification Systems," *Technical Bulletin No. 675,* August 1994, 88 -91.

[55] Douglas Pryke *et al.,* "Environmental Improvements at Grand Prairie and Ecosystem Response," *Pulp & Paper Canada*, **96(11)**: 42 (1995).

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[57] Andrew A. Meharg and Daniel Osborn, "Dioxins released from chemical accidents," *Nature*, **375**: 353-354 (1995).

[58] Based on toxic equivalence factors (TEF) developed by EPA, TCDD has a TEF of 1.0 as the most toxic member of the dioxin and furan family. TCDF and the dioxins and furans with 6 chlorines (hexachlorodibenzo-p-dioxins and hexachlorodibenzofuran) have TEFs of 0.1. The TEFs of the hepta- and octa- CDD and CDF compounds are 0.01 and 0.001 respectively. [U.S. EPA, *REVIEW DRAFT: Estimating Exposure to Dioxin-Like Compounds, Volume I: Executive Summary* (Washington, DC: Office of Research and Development, EPA Report No. EPA/600/6-88/005Ca, June 1994), 3. (REVIEW DRAFT: *Estimating Exposure to Dioxin-Like Compounds, Volume I, hereafter)* .

[59] U.S. EPA, Office of Research and Development, *REVIEW DRAFT: Estimating Exposure to Dioxin-Like Compounds Volume*, 20, 24.

[60] Jean Renard, International Paper, presentation to the Paper Task Force, September 1, 1994.

[61] *Federal Register*, **58**: 66083 (1993).

[62] U.S. EPA, *Regulatory Impact Assessment,* 7-8.

[63] Penny Lassiter, Office of Air and Radiation, U. S. EPA Raleigh, NC, telephone interview, 10 November 1995.

[64] NCASI emissions for total HAPs is the sum of the emissions of the individual HAPs measured in the study. NCASI collected the raw emission data for each HAP as a concentration, and then converted the concentration to pounds per oven-dried ton of pulp using the molecular weight of each compound. NCASI measured total VOC emissions using an EPA test for these emissions. The concentrations of the raw total VOC data are converted to mass emissions using the molecular weight of carbon rather than the molecular weight of the individual compounds. The EPA method is used to measure VOC emissions for regulatory purposes. Richard Storat notes that this test is known to have a poor response to certain compounds such as methanol and formaldehyde. [Richard Storat, vice president, economics and materials, American Forest & Paper Association, letter to David Refkin, 26 May 1995, 10.] Thus, it is possible that this test underestimates the actual VOC emissions.

[65] NCASI, "Volatile Organic Emissions from Pulp and Paper Mill Sources - Part V: Kraft Mill Bleach plants," *Technical Bulletin No. 679,* October 1994, 117, 125.

[66] U.S. EPA, *Regulatory Impact Assessment,* 7-11.

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[68] Bruce McKague, comments at the NCASI Technical Workshop on Chlorinated Organic Substances, Washington, DC, February 17, 1994; Bruce McKague, Marianne Jarl and Knut P. Kringstad, "An up-to date list of compounds identified in bleachery effluent as of January 1989," ÅF-IPK, 1989.

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[75] R.J. Shimp, and J.W. Owens, "Pulp and Paper Technologies and Improvements in Environmental Emissions to Aquatic Environments," *Toxicol. and Environ. Chem*., **40**: 224 (1993).

[76] Jukka Tana, *et. al.,* "Assessing impacts on Baltic coastal ecosystems with mesocosm and fish biomarker tests: a comparison of new and old wood pulp bleaching technologies," *Sci. Total Environ*., **145**: 214 (1994).

[77] Ibid.

[78] Jocelyn Woodman, *Pollution Prevention Technologies for the Bleached Kraft Segment of the U.S. Pulp and Paper Industry* (Washington: U. S. EPA Office of Pollution Prevention and Toxics, EPA/600/R-93/110, 1993), p. 2-4.

[79] Robert Shimp, section head, paper products division, environmental safety and external relations, Procter & Gamble, letter to Linda Fransen, Perseco, 9 June, 1995.

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[82] NCASI, "Effects of Chlorine Dioxide Substitution on Bleach Plant Effluent BOD and Color," *Technical Bulletin No. 630*, March 1992, 3.

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[100] Betsy Bicknell, Douglas Spengel and Thomas Holdworth, *1995 International Non-Chlorine Bleaching Conference,* 14.

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[103] John Morgan, "Mill Experience with 100% ClO_2 Substitution Bleaching," *Proceedings of the 1993 Non-Chlorine Bleaching Conference* (San Francisco: Miller Freeman Inc., March 1993), 5; Alan E.

Stinchfield and Michael G. Woods, "Mill Experience with Reduction of Chlorinated Organic Compounds from Bleached Kraft Mills Using Complete Substitution of Chlorine Dioxide for Chlorine in the First Bleaching Stage," NCASI Technical Workshop on Effects of Alternative Pulping and Bleaching Processes on Production and Biotreatability of Chlorinated Organics, Washington, DC, 17 February 1994, p. 5. The estimate of the high level of AOX from the bleach plant is based on the final effluent AOX number from Morgan source and using treatment efficiency of 22% as reported by Stinchfield and Woods.

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[105] Rudolph Thut, "Performance of Weyerhaeuser Bleached Kraft Mills with Extended and/or Oxygen Delignification and 100% Chlorine Dioxide Substitution," *NCASI Technical Workshop on Effects of Alternative Pulping and Bleaching Processes on Production and Biotreatability of Chlorinated Organics*, Washington, DC, 17 February, 1994, 4.Jean Renard, International Paper, presentation to the Paper Task Force, 1 September 1994.

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[110] Thomas L. Wiesemann, "The Environmental Impact of Chlorine Dioxide Substitution," *NCASI Technical Workshop on Effects of Alternative Pulping and Bleaching Processes on Production and Biotreatability of Chlorinated Organics*, Washington, DC, February 17, 1994, Table 15.

[111] Alan E. Stinchfield and Michael G. Woods, "Mill Experience with Reduction of Chlorinated Organic Compounds from Bleached Kraft Mills," 5.

[112] Keith Solomon, Harold Bergman, Robert Huggett, Donald MacKay and Bruce McKague, "A Review and Assessment of the Ecological Risks Associated with the Use of Chlorine Dioxide for the Bleaching of Pulp," *1994 International Pulp Bleaching Conference*, 149.

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[114] Alberta Department of Environmental Protection; Alan Stinchfield and Michael Woods, "Reducing chlorinated organic compounds from bleached kraft mills through first stage substitution of chlorine dioxide for chlorine," *Tappi Journal*, **78(6):** 120 (1995).

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[120]U.S. EPA, *REVIEW DRAFT: Estimating Exposure to Dioxin-Like Compounds*, 19-20.

[121] These levels may be high because none of the 7 bleached kraft mills in Maine were operating traditional ECF bleaching processes when the fish sampling was done. The tissue levels, however, are not historical. The rivers in Maine scour the bottom so little sediment builds up. Dioxin concentrations in the trout and bass in Maine's rivers reach equilibrium concentrations in about 1 year. [Peter Washburn, staff scientist, Natural Resources Council of Maine, personal communication.]

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[128] Dick Erickson, "Closing Up the Bleach Plant", Appendix B.

[129] Ed Clem, vice president, Environmental Affairs, Champion International, personal communication, June 9, 1995.

[130] Tibor Kovacs, group leader, Aquatic Biology, PAPRICAN, personal communication, June 9, 1995.

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[135] Roland Lövblad and Jan Malmström, "Biological Effects of Kraft Pulp Mill Effluents - A Comparison Between ECF and TCF Pulp Production," *Proceedings of the 1994 International Non-Chlorine Bleaching Conference*, (San Francisco: Miller Freeman, Inc., March 1994).

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