Chapter 1

Introduction, Summary, and Findings

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PURPOSE AND SCOPE

"Dioxin" is the term used in referring to the family of 210 chlorinated chemicals known as chlorinated dibenzo-para-dioxins and chlorinated dibenzofurans. The most toxic member of this large family of compounds is 2,3,7,8 -tetrachloro-p-dibenzodioxin (2,3,7,8 -TCDD or TCDD); the closely related compound 2,3,7,8 -tetrachloro-dibenzofuran (2,3,7,8 -TCDF or TCDF) is believed to be about one-tenth as potent. Both of these chemicals can be formed during the manufacture of bleached wood pulp if chlorine is used as a bleaching agent. The amount of TCDD and TCDF formed in the bleaching process is measured in parts per trillion (ppt). The relative toxicity of these chemicals is measured in ppt and expressed as "Toxic Equivalents" (TEQs) using TCDD as the standard. TCDD is considered to be highly toxic based on laboratory animal experiments and has been linked to malignancies, birth defects, and physical deterioration in animals, Evidence of human health effects is less certain and remains a contentious issue among scientists. The U.S. Environmental Protection Agency (EPA) classifies it as a "probable human carcinogen."

The release of EPA's National Dioxin Study in 1987 focused attention on evidence that showed a pattern of dioxin concentrations in stream bottom sediment and fish below pulp mill waste outfalls. Subsequent studies by the paper industries and government agencies in North America and Europe have confirmed that detectable amounts of TCDD and TCDF are produced and released into the environment at many bleached kraft pulp mills. Measurements of dioxin levels in the three sources of pollution (pulp, effluent, and sludge) are being conducted at all U.S. chemical pulp mills using chlorine bleach under the joint sponsorship of EPA and the American paper industry. The results of these studies and others underway in Canada and Europe will contribute much more to the information base now available, but final results are months away.

Bleached wood pulp is used in paper products such as writing and printing papers, rayon, tissues, towels, disposable diapers, food packaging, and a myriad of other products. Paper is used so widely in modern societies that every person comes in contact with bleached paper products almost daily. The knowledge that TCDD and TCDF are produced and released during the manufacture of chlorine-bleached kraft pulp has prompted action by the Federal agencies charged with protecting health and the environment and has stimulated research by a paper industry faced with increasing public concern and, as a consequence, possible regulatory action.

Environmental and consumer groups have organized an international action program to inform the public, prompt consumer action, and stimulate political and regulatory action in the pulp-producing countries of North America and Europe. The United Paperworkers International Union, the labor union that represents many of the paper mill employees in North America, and the National Institute for Occupational Health (NIOSH) are monitoring the potential health impacts of exposure of workers to dioxin in pulp and paper mills.

This study reviews what is known about the production and fate of TCDD and TCDF and other associated chlorinated compounds during the course of pulp bleaching and brightening. The study is specifically aimed at assessing the state of pulping and bleaching technologies that show promise for reducing the amount of those chemicals resulting from the manufacture of bleached kraft pulp, such as extended delignification, oxygen delignification, the use of bleaching chemicals that might substitute for some or all of the chlorine commonly used, modifications of the timing, amount, and operating conditions of the chlorine bleach sequence, and a review of pulping and/or bleaching technologies that are not yet commercially available, but might be in the future.

Because this is a technical background report, neither an assessment of policy options related to the need for regulatory action, nor the form such regulations might take, are included. Furthermore, this assessment assumes—based on past trends and industry projections—that a strong demand for high-brightness bleached pulp and paper products will continue in the future. Should the public boycott or avoid the use of bleached paper products in the future because of a perceived health risk, the paper industry would have to adjust to the changing markets within its own constraints.

Markets for unbleached hygienic paper products, disposable diapers, coffee filters, and milk cartons, for example, have developed in Sweden where "environment-graded" or "environment-positive" lines of unbleached paper products are retailed along with bleached grades. Recently, the Canadian pulp and paper industry has agreed to reduce the amount of dioxin in paper stock used for milk containers after Health and Welfare Canada, a government agency, discovered trace amounts of dioxin leaching into milk from plastic-coated paper cartons. The pulp and paper industry claims that paper products requiring high strength and long-term durability generally must be made with a highly bleached pulp, and industry analysts believe that this will likely continue to be a major proportion of the pulp produced.

Market pulp is a commodity traded widely in world markets. The possibility exists that some countries in the future may impose limits on the amount of residual chlorine compounds or dioxin in pulp and paper products that can be imported. If similar collective action were to be taken by a large number of trading partners, such as the European Economic Community or a coalition of Pacific Rim countries, a significant portion of North America's export market could be affected. If such trade restrictions were broadly adopted, it could, for practical purposes, impose de facto international performance standards on those firms wanting to compete in international markets.

OTA convened a workshop in November 1988 to discuss the latest information regarding three aspects of dioxin and bleached wood pulp manufacture:

1. What is known about the distribution and effects of TCDD and TCDF resulting from environmental releases by pulp mills?
2. What is known about the amount of residual TCDD and TCDF in paper products, and what is the level of risk to consumers and mill workers?
3. What is the current understanding of the precursors that react with chlorine to form TCDD and TCDF, and what is known about the means to reduce their formation?

As a result of the workshop, we were impressed by how fast knowledge about TCDD and TCDF in bleached wood pulp is accumulating. This report is on] y a "snapshot" of the technology and knowledge about the formation of dioxin and possible means to reduce it as of December 1988.

THE U.S. PULP AND PAPER INDUSTRY

The United States leads the world in per capita paper consumption. In 1986 U.S. consumers used over 660 pounds of paper products per person.[1] This new record of paper consumption continues the steady increase in the domestic use of paper that saw per capita consumption rise about 16 percent between 1976 and 1986. Paper, which is indirectly correlated with gen-

[1] American Paper Institute, *1987 Statistics of Paper, Paperboard& Wood Pulp* (New York, NY: Associated Press International, 198'7), p. 2.

eral economic activity, is currently being consumed at the rate of about 21,000 tons per billion dollars of the real gross national product (GNP) generated. For a variety of reasons, including the reduction of solid waste, efforts to recycle scrap paper are expanding, particularly in urban areas.

Nearly 73 million tons of paper, board, and construction board were produced in the United States in 1986.[2] Although 4.8 million tons of paper products were exported by U.S. producers, almost 12 million tons were imported for domestic consumption. Most of the imports originated in Canada and were newsprint. More than 70 percent of U.S. exports and 80 percent of imports in 1987 were bleached or semi-bleached pulps.[3]

Pulp products valued at $3.9 billion were shipped from U.S. pulpmills in 1987. The paper and allied products industry (SIC 26) employed over 674,000 persons in 1986, with about one-third of those directly involved in the production of paper and pulp (SIC 261, 262, 266).[4] In general, pulp mills have tended to concentrate in the South and Northwest near major sources of wood, while allied industries and conversion facilities are more broadly distributed near primary markets.

Future prospects for the pulp and paper industry are bright. In the Pacific Rim countries where industrial expansion is expected to increase dramatically, forest-deficient countries like Japan, Korea, and Taiwan are considered large potential markets. The United States and Canada, with their vast forest resources, their established industries, and technological capacity, are well positioned to take advantage of new export markets. However, international competition for new markets is sharpening, with overseas suppliers in Brazil, Portugal, Spain, Morocco, and South Africa expanding their capacity.

SUMMARY

The Pulp and Paper Making Process

The manufacture of pulp and paper involves the separation and purification of cellulosic wood fibers from which paper is formed. About half of the wood raw material is cellulosic fiber, and half is lignin, hemicellulose, and other extractive compounds that cement and strengthen the fibers. The pulping process involves either the use of chemicals, heat, and pressure in a digester to dissolve the lignin and free the fibers from one another or, in the case of mechanical pulp and chemical-mechanical pulp, the abrasion of wood in a grinder or refiner to physically tear the fibers apart.

Pulping and bleaching technology must be matched to the quality and characteristics of the pulp and paper to be produced. No single pulping or bleaching process can produce pulp suitable for all uses.

To produce purified cellulose and white pulps, lignin and other colored extractives carried forward from the digester must be removed or brightened in successive bleaching stages using chlorine and/or other oxidative chemicals. It is in the bleaching processes where most chlorinated organic contaminants, including dioxin, originate. A wide range of bleaching sequences and caustic washing stages may be used to bleach and brighten pulp. The choice of which bleaching agents and in what sequence is generally determined by pulp characteristics desired, such as brightness and strength, balanced against capital and operating costs.

[2] Ibid.

[3] U.S. Department of Commerce, *1988 U.S Industrial Outlook* (Washington, DC: International Trade Administration, 1988), p. 6-3.

[4] American Paper Institute, op. cit., note 1, p. 54. NOTE: “S[C”r~fers[0“S~d~d Industrial Code,” a classification of U.S. industries used by the U.S. Department of Commerce.

Several pulping [illegible] precommercial or pilot [illegible] are not "new" [illegible] new because they have not yet been accepted by the industry. [illegible] processes rather than [illegible].

New pulping technologies are emerging, but their acceptance will depend on efficiency, pulp quality, cost effectiveness, or other factors that make them competitive with conventional technology. To the extent that new pulping systems might reduce the amount of residual lignin carried over to the bleaching process, the amount of chemical bleaching required to attain the desired brightness might be reduced and subsequently the amount of chlorine used as a bleaching agent trimmed.

Environmental Considerations

Effluents from bleached pulp mills contain a variety of substances, some of which are known or suspected of being toxic, genotoxic, mutagenic, or teratogenic. Chlorinated organics, including TCDD and TCDF, that appear to be produced in the chlorine bleaching and delignification processes, are of particular concern. The composition of bleaching effluent is extremely complex and varies widely from mill to mill. The chlorinated components of the waste stream consist of a variety of compounds, including simple phenols, high and low molecular weight polymers, and neutral and acidic materials from the breakdown of the phenolic rings in lignin. An average North American pulp mill produces between ***35*** and ***50*** tons of chlorinated substances daily. Greenpeace International, the Environmental Defense Fund, and other environmental organizations advocate immediately minimizing and eventually eliminating the use of chlorine in order to avoid additional releases of these compounds into the environment through effluent, sludge, or via paper products.

[illegible] of TCDD and TCDF can be [illegible] many other chlorinated [illegible], when wood pulp is [illegible] chlorine gas.

About 10 percent of the total solids in the waste streams of bleaching plants contain chlorinated derivatives, but this varies among mills depending on the degree of filtration. Some European countries, Sweden and the Federal Republic of Germany in particular, have imposed restrictions on the amount of total organically bound chlorine (TOC1) that they will allow their pulp and paper industry to discharges Sweden has cut the amount of allowable TOC1 discharge more than half, from the 5 to 6 kilograms per metric ton (kg/t) of pulp normally produced with conventional chlorine bleaching, to 2 kg/t. Oxygen delignification and chlorine dioxide substitution have been the technology of choice to meet Sweden's environmental requirements. The National Swedish Environmental Protection Board hopes to reduce TOC1 to 0.1 kg/t by 2010 and to 1.5 kg/t by 1992. With further reductions in allowable discharges, the Swedish industry may need to adopt closed-cycle processes to eliminate chlorinated discharges entirely.

[illegible] Federal Republic of Ger-[illegible] from regulating pulp [illegible] limits on chemical [illegible] limits on the amount of [illegible] released per ton of [illegible] produced. This will have a forcing

[5]Between 250 and 300 chemicals have been identified in pulp mill effluents. Many of them arc chlorinated organic compounds. Sce Lcena R. Suntio, Wan Ying Shiu, and Donald Mackay, "A Review of the Nature and Properties of Chemicals Present in Pulp Mill Effluents," *Chemosphere*, vol. 17, No. 7, 1988, pp. 1249-1290. TCDD and TCDF make up a very small fraction of the total organochlorine emissions.

effect on the pulping, bleaching, and waste treatment technologies used in those countries.

In 1988 the Board also considered the overall problem of dioxin in the Swedish environment and concluded that standards established for reducing TOC1 would suffice to reduce the dioxin levels from bleached pulp as well. Chlorinated organic effluents from pulp and paper manufacture have created environmental problems in coastal waters and estuaries of the Baltic Sea, particularly in the enclosed Gulf of Bothnia. Unlike U.S. pulp mills that use secondary biological sewage treatment technologies to treat waste effluents, mills in Sweden, some in Finland, and many in Canada do not use comparable treatment methods before discharging into the environment. Biological treatment can remove large amounts of chlorinated contaminants (particularly those that adhere tightly to sediments such as TCDD and TCDF) from mill effluents when operated properly. Biological treatment transfers the contaminants from the water and concentrates it in the sludge. The sludge must then be disposed of in a safe and acceptable manner. Biological treatment systems require constant attention to ensure that they are working efficiently.

U.S. environmental regulations that limited the release of "conventional" pollutants from pulp mills induced the domestic industry to install secondary biological waste treatment plants to meet the standards. Most plants in Europe and many in Canada do not have secondary waste treatment.

The Federal Republic of Germany will begin tightening restrictions on the discharge of chlorinated organics in 1989. Maximum allowed discharges of organochlorines will be 1.0 kg/t of bleached pulp under the new regulations. Until recent] y, West German regulations for pulp mill discharges have not been overly strict. Fees levied on discharged amounts of oxygen demand, solids, and measures of toxicity to fish have allowed the German industry to "buy" the right to pollute.

Chlorinated organic residues from pulp bleaching have caused less concern in North America where little research into adverse impacts on fisheries and aquatic biota has been conducted. There is ample experimental evidence, however, that pulp mill effluents, unless adequately treated, can be toxic to fish and some chlorinated compounds may ultimately find their way through the food web. Dioxin has been shown to be extremely toxic to fish at very low concentrations under controlled laboratory experiments and has been linked to periodic reductions in reproductive rates of some bird species. U.S. mills, unlike their European counterparts, have installed extensive biological treatment systems to reduce the biological and chemical oxygen demand (BOD and COD) of their waste effluents before discharging them into streams. U.S. environmental requirements for the issuance of a discharge permit for conventional pollutants, such as BOD, COD, and suspended solids, and toxicity tests on mill effluents make biological waste treatment a preferred technology for U.S. mills.

Dioxin levels in some whole fish sampled in the National Dioxin Study and in other samples taken below pulp mills exceeded the safe levels prescribed by the FDA. It is known that fish can accumulate dioxins in their bodies (concentrating mostly in the inedible body parts) many thousands of times more than the concentrations of dioxin in the receiving waters. Ingestion by eating contaminated fish may be the source of the public's greatest exposure to dioxin resulting from pulp manufacture.

The detection of dioxin in some fish samples reported in EPA's National Dioxin Study has raised concern about the possible effects on human health. Less than 20 percent of the *randomly* selected sites sampled by EPA in the study showed detectable quantities (more than one part per trillion [ppt]) in whole fish samples. Other samples collected at over 300 *regional* sites selected by EPA for high probability of dioxin contamination showed that nearly one-third of the rivers, lakes, coastal waters, and estuaries contained fish with detectable amounts of dioxin that ranged up to 85 ppt—significantly higher than the 25 ppt determined to be unsafe by the Food and Drug Administration (contained in edible fillets, not in whole fish)-but it is not certain that pulp mill waste was the source of all contamination. Only 4 of 57 *estuarine and coastal* sites sampled in the National Dioxin Study had detectable levels of dioxin in fin fish or shellfish. Based on laboratory tests, fish have been shown to accumulate dioxin in their bodies at rates approximately 20,000 to 85,000 times the concentrations to which they are exposed in water. Fishing has been prohibited in several rivers because of dioxin levels, and advisories have been issued by Wisconsin, Maine, and Louisiana warning of the possible risks of eating contaminated fish.

A screening analysis of pulp waste at five bleached kraft pulp mills, which was conducted jointly by EPA and the U.S. paper industry, and other research in Europe and Canada clearly links the formation of TCDD and TCDF to the chlorine bleaching process. TCDD was detected in seven of nine bleached pulps sampled, some with levels as high as 51 ppt. TCDF, which is less toxic than TCDD, was found in eight of nine pulps sampled, with levels ranging up to 330 ppt.

Dioxin was detected in wastewater at four of the five mills, but concentrations varied greatly among the mills sampled. The highest levels of TCDD and TCDF were associated with waste from the caustic extraction stage, which is designed to remove the dissolved materials after the chlorine treatment. EPA and the paper industry are currently surveying 104 additional mills to better determine the scope and extent of dioxin and furan formation. Detailed analyses of TCDD levels and bleaching processes at 25 pulp mill bleach lines will be conducted in the course of the study.

[illegible] TCDD or TCDF [illegible] Compared to other common sources of daily ambient exposure to dioxin, dermal exposure from paper products seems to be comparatively small. Estimates of the cumulative exposure from multiple sources must be considered. An Interagency Task Force led by EPA is currently attempting to do this.

The detection of TCDD and TCDF in bleached pulp samples raised concern about whether residual dioxin was being carried forward into finished paper products. The National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI), the industry's environmental research arm, commissioned an assessment of the potential risks to human health from skin exposure to a variety of paper products, including disposable diapers, facial tissue, toilet tissue, sanitary napkins, coffee filters, and paper towels. The assessment concluded that TCDD equivalents in all products tested presented a lifetime cancer risk of less than one in a million.

Environmentalists note that NCASI's assessment only considered the risks for 2,3,7,8-TCDD and 2,3,7,8-TCDF without examining the risks from the several hundred other chlorinated byproducts that are also found in paper products, and that NCASI failed to consider the cumulative risk of using a wide range of paper products daily. Environmentalists also fault NCASI for not using appropriate testing procedures for evaluating the possible enhanced mobility of dioxin when in the presence of lipids, solvents, and fats, such as encountered when using paper towels for cooking or when using creams and baby oils with disposable diapers.

OTA learned at its dioxin workshop that there is considerable disagreement about the validity of the testing protocols for determining the rate of migration of dioxin from paper products and into the human body. For instance, there are widely differing opinions about how to estimate the effect of urine leaching from disposable diapers into the skin of babies, and how to simulate the environment of a tampon in determining the movement of dioxin into a woman's body. Without standard protocols, disagreements over the meaning of dioxin risk data leaves OTA with no means to evaluate the industry's findings and conclusions. Evaluation of these testing techniques is beyond the scope of this assessment.

Agreement is also lacking on how to express levels of risk. Does one accept a one in a million risk of cancer as did the U.S. paper industry in its study of risks from dermal exposure to dioxins, or should the acceptable risk be one in a thousand? There are *no* Federal regulatory standards. Arbitrary levels of risk are used for convenience, and experts differ over the most appropriate levels to use.

Semantics also contribute to the confusion: Should dioxin exposure levels be expressed as "virtually safe dose," which implies that there "is a level of exposure at which the cancer risk is zero," or should the term "risk specific dose" be used since it does not imply that there is any dose above zero that is "safe"?

Couple the uncertainties over testing protocols with disagreement over levels of acceptable risk, and add to it the lack of consensus about the potency of dioxin to humans, and a confused picture is presented to those attempting to gauge the danger of dioxin from pulp manufacture and paper use.

OTA is aware of no published studies that have attempted to define worker exposures to dioxin in paper mills using environmental measurements or biological exposure measurements, such as serum or fat TCDD/TCDF concentrations. The National Institute of Occupational Safety and Health (NIOSH), the Federal agency charged with occupational and health research, is currently developing personal exposure monitoring methods to address pulp and paper workers' exposure to dioxin.

EPA is currently coordinating an Interagency Task Force on Dioxin in Paper aimed at gauging the cumulative risk of all of the media that could contribute to human exposure. Other cooperating agencies include the Food and Drug Administration and the Consumer Product Safety Commission (CPSC). The interagency effort was characterized by an EPA official at the November 1988 OTA dioxin workshop as an effort to "determine whether there is a risk—not a 'gold plated' risk assessment," and a "snapshot in time" as to the risk aimed at determining whether regulation is needed. The interagency study will build on both the EPA/Industry 104-mill study and estimates of migration rates of dioxin from paper products. It will include an assessment, based on product-use scenarios, of technologies that could reduce dioxin exposure.

OTA found that, as with many other Federal activities, the analytical and regulatory authority for dealing with dioxin in paper is fragmented among several agencies, none of which have clear responsibility for dealing with the problem in its entirety. While EPA has jurisdiction over water pollution and dioxin in pulp (dealt with in two separate offices), FDA has responsibility for regulating dioxins in coffee filters and sanitary napkins, and CPSC has responsibility for dioxin in disposable diapers, paper towels, facial tissues, and toilet tissues.

The lack of published independent Federal research on the risks associated with dioxin in paper products and the absence of government information on paper worker's environmental exposure to dioxin required OTA to rely almost wholly on industry-sponsored research. The paucity of government information on workers' risk and exposure to dioxin in paper products may change in the future as a result of the Interagency Task Force on Dioxin in Paper mentioned above, but in the meantime we have only industry information available to evaluate the potential risks from dioxin in paper.

Pulp Bleaching Technology

About 10 percent of the lignin found originally in wood is carried over from the chemical digestion process to the bleaching stages in kraft mills. This residual lignin must be substantially reduced if pure cellulose products or bright paper are to be produced. The less lignin retained in the pulp as it leaves the digester, the less bleaching needed. There are limits, however, as to how much digestion wood fibers can endure without sacrificing pulp strength and paper durability or significantly reducing pulp yield.

The tendency has been to bleach more pulp as the demand for products using bleached paper increases. Most of the bleached pulp has been produced by the kraft chemical process. Very little mechanical pulp has been bleached in the past, but now it is increasing at twice the rate of chemical pulp bleaching worldwide. Mechanical pulp is not normally bleached with chlorine gas but with hydrogen peroxide or sodium hydrosulfide.

Bleaching is a continuation of the delignification process and is used to brighten and purify the wood pulp. The purer the cellulose and brighter the paper, the less lignin retained, and the longer the paper will last without yellowing and becoming brittle. Chlorine gas has become the preferred bleaching agent because of its relatively low cost and high effectiveness. However, a number of other bleaching chemicals are also used, including hypochlorite, chlorine dioxide, oxygen, and hydrogen peroxide. Ozone has also been tried under experimental conditions, but is not yet commercially available. Each has its advantages and disadvantages, and several are usually used in sequence to achieve the final result. Between bleaching stages caustic chemicals are often used to remove the dissolved lignin and wash the fibers before they are subjected to additional bleaching. It is apparently during this extraction that much of the dioxin created by chlorine bleaching finds its way into the waste stream.

By reducing or eliminating the use of chlorine gas in the bleaching process, the amount of chlorinated organic waste products and dioxin can be reduced. The reduction or elimination of organic precursors that form dioxin can also reduce the amount of dioxin produced. Little is currently known about these precursors—although knowledge is accumulating rapidly—and more research is needed in this area.

It has been shown that by reducing the use of chlorine gas in the bleaching process, the amount of chlorinated organic residues and contaminates can be reduced. Oxygen delignification shows some promise for reducing the amount of lignin carried with the pulp to the bleach process, thus reducing the amount of chlorine gas needed to bleach the pulp to the desired brightness. Current commercial oxygen delignification technology can reduce the use of chlorine gas by 40 to 50 percent. Further reductions in the use of chlorine by more intense oxygen delignification is limited by severe losses in pulp yield and strength properties. Pretreatment of the pulp with nitrogen dioxide before oxygen treatment shows promise for increased delignification before bleaching.

The cost advantage that chlorine gas once had over many other bleaching agents does not apply to oxygen. If the U.S. pulp and paper industry is required to reduce the amount of chlorinated organics and dioxin produced in bleaching pulp, oxygen may become a partial substitute for chlorine because of its low operating cost. Capital cost for oxygen treatment is very high, however, and installation of oxygen delignification in existing mills can reduce production capacity as much as 4 or 5 percent. Any evaluation of the comparative costs of oxygen technology with other delignification systems should consider both capital costs, life-cycle costs based on operating costs and depreciation, and gains and losses in productivity and quality. Such analyses were not made by OTA in this study.

Technologies for Reducing Dioxin

There are several ways to reduce the amount of pollution contributed by bleach plants. These include:

- further delignification of pulp before bleaching;
- improved washing of the unbleached pulp (brownstock);
- substitute nonchlorinated bleach agents;
- substitute chlorine dioxide for some or all chlorine gas;
- apply multiple additions of chlorine in split charges instead of using a single, massive charge (low chlorine multiple);
- improve chemical mixing with the pulp;
- adjust the acidity of the unbleached stock before adding chlorine;
- use "cleaner" oil-base defoamers that do not contain dioxin precursors;
- remove dioxin precursors prior to treatment of the pulp with chlorine; and
- improve secondary waste treatment and waste-disposal practices.

Pretreatment before bleaching can reduce the amount of chlorine or other bleaching chemical used. Technologies for prebleach delignification include: 1) extended delignification, 2) oxygen delignification, 3) pretreatment with nitrogen dioxide before oxygen delingification (PRENOX allows more lingin to be removed without damaging fibers), 4) pretreatment with other chemicals such as chlorine dioxide, and 5) extraction with sodium hydroxide supplemented with oxygen and hydrogen peroxide. Only extended delignification and oxygen delignification are currently used commercially.

Other technologies used to conserve water and reduce energy consumption may also help reduce the amount of chlorinated products in the waste stream:

- recycle process water from the chlorination stage (although this may actually compound the dioxin problem),
- use countercurrent washing systems after chlorination, and
- reduce water use by using higher ratios of fiber pulp to water (higher consistency).

Elimination of chlorine in the bleach sequence combined with internal recycling of process water aimed at developing a "pollution-free" pulping system seems to offer a good strategy over the long term, but has not yet been adopted for commercial use.

There are several possible ways to reduce the use of chlorine gas in bleaching to high pulp brightness: 1) substitute chlorine dioxide for part or all of the chlorine, 2) use hydrogen peroxide or ozone (experimental only), and 3) extraction between bleach stages with sodium hydroxide, supplemented with oxygen and hydrogen peroxide.

It is believed that if the use of chlorine gas is reduced or eliminated in the bleaching process, the amount of TCDD and TCDF formed will be lowered or eliminated along with other chlorinated organics. However, the relationship is not linear, and other factors, such as mixing efficiency, have significant effects on the relationship. Oxygen is one of the most promising bleaching chemicals for displacing some of the chlorine used in the bleaching cycle. In no case thus far has oxygen been able to completely eliminate the need for chlorine.

Chlorine dioxide, a more efficient oxidant than chlorine, can be substituted for substantial amounts of chlorine gas. The use of chlorine dioxide in conjunction with chlorine gas is increasing at U.S. mills. It has been demonstrated that substitution of chlorine dioxide for some optimum portion of chlorine gas can significant] y reduce the formation of TCDD and TCDF. However, the effects of chlorine dioxide substitution on the formation of other chlorinated compounds are not known.

It may also be possible to reduce the amount of TCDD and TCDF formed by chlorine bleaching if the acidity (pH) of the reaction is controlled closely and/or if the chlorine is applied in smaller, multiple charges instead of one large charge. Further experimentation is needed to verify the potential of these process modifications.

Recent research has also shown that the amount of dioxin can be reduced by lowering the acidity (raising the pH) of the pulp before chlorination, by applying the chlorine charge in three parts instead of one shot, and by using chlorine dioxide after an initial charge of chlorine gas. A very recent discovery by scientists at the Pulp and Paper Institute of Canada has identified oil-based defoamers as one possible source of the precursors that form dioxin when chlorinated. As a consequence, the U.S. industry and chemical suppliers are currently seeking cleaner oil-based defoamers.

Precursors must be present for TCDD and TCDF to be formed by reaction with chlorine. There are a number of possible sources: 1) natural constituents in the wood, 2) contaminants in the pipes and [illegible] precursors that can form TCDD when chlorinated. Chemical suppliers and the pulp and paper industry are searching for clean defoamers, but none are currently available that can be used effectively for brownstock washing.

Defoamers are added to the unbleached pulp in small amounts to improve washing. If a defoamer is made from used oil contaminated with unchlorinated dioxins (DBD) and furans (DBF), these precursors convert to their chlorinated forms as TCDD and TCDF when exposed to chlorine gas. The United States regulates the use of contaminated recycled oil, so further investigation is needed to determine whether defoamers are a problem for U.S. mills using domestically produced products. Recent investigations by American scientists using testing protocols more sensitive than those used in Canada have raised doubts as to whether any oil-based defoamers—whether made from either virgin, hydro-treated oil, or used oil—are free of contaminating precursors.

Water-based defoamers are also available, and tests show them to be free of DBD and DBF precursors. Unfortunately, while water-based defoamers can be used at other washing stages in the mill, they are not effective for washing brownstock. The use of "cleaner" defoamers is another option for reducing some of the dioxin produced in the bleaching process, but more research and development may be needed to develop suitable products.

Oxygen delignification technology was discovered in 1952, and the first commercial unit was installed in the 1960s. Since then, oxygen technology has advanced steadily until it is now considered a mature and proven process. In 1988, world installed capacity using oxygen delignification is expected to exceed 10 million metric tons per year. Several manufacturers of pulp and paper equipment market oxygen delignification systems. Over 50 oxygen units have been installed worldwide. About half the oxygen capacity is in Scandinavia and Europe, one-fifth is in Japan, and one-fifth is in North America. About 92 percent of the oxygen bleaching capacity is installed in kraft mills, but a number of sulfite mills—mostly in the Federal Republic of Germany—have also installed oxygen delignification units.

Oxygen can also be used in combination with extended digestion (modified cooking). By modifying the chemical addition and allowing it to cook longer, the amount of residual lignin in the pulp can be reduced prior to bleaching. Further pre-bleaching with oxygen can produce pulp with even lower amounts of lignin. With prebleached pulps of low lignin content, it may be technically possible to eliminate the use of chlorine gas in the bleaching process if chlorine dioxide is used as a substitute.

No reliable data exist that directly link the reduction of TCDD and TCDF wholly to oxygen delignification, and in some cases oxygen pulps have been shown to contain some TCDD and TCDF. There is, however, substantial evidence that oxygen delignification after pulping and before the first bleaching stage *can reduce* the amount of chlorinated organics produced in proportion to the reduction in residual lignin. At this time, too few comparative analyses have been made of dioxin in oxygen-treated pulps v. that in conventional pulp to absolutely support the hypothesis that oxygen bleaching substantially reduces TCDD and TCDF in bleached pulps, although unpublished EPA data based on three mills sampled in 1988 seem to support this hypothesis.

There is no "silver bullet" for reducing the TCDD and TCDF in bleached pulp. Several technologies and/or process modifications may be used individually or in combination. The choice of technologies and their effectiveness depends on the existing mill configuration and the quality of the pulp produced. New mills have more flexibility.

Modem mills are designed to match the capacity of the chemical recovery plant with the planned production capacity of the mill. The addition of an oxygen delignification stage increases the volume of effluent that must be handled by the chemical recovery plant. In new mills recovery plants can be designed to handle the additional load, but retrofitting an existing mill with an oxygen delignification system can result in overloading the chemical recovery capacity. If a larger size recovery furnace or evaporators are required, the additional capital expense may make oxygen delignification a less attractive alternative for economic reasons. It is estimated that adding an oxygen stage to a mill whose chemical recovery plant is operating at full capacity will reduce the productivity of that mill 4 to 5 percent.

Given a range of equally effective technologies to reduce the use of chlorine gas, capital and operating costs may determine the most cost-effective strategy for reducing the amount of chlorinated organic chemicals produced by pulp mills. Although operating costs may be lower if oxygen delignification is used to replace some of the chlorine gas now used in the bleach cycle, the capital cost of oxygen systems is large. Both capital costs and operating costs must be considered in a balanced assessment. Furthermore, cost factors will differ from mill-to-mill, making generalizations difficult. OTA did not attempt to assess these costs. On the other hand, by using "cleaner" defoamers, coupled with substitution of chlorine dioxide for chlorine, it may be possible to achieve much lower levels of TCDD and TCDF in pulp. Whether or not this would also lower the level of other chlorinated compounds is uncertain.

Additional control of suspended solids that bind TCDD and TCDF by adding clarifiers or sorbents to the biological waste treatment systems, and/or dechlorination of bleach plant waste might prove effective in removing dioxin from effluent at some mills. Dioxin-bearing sludge must then be disposed of in a safe and appropriate manner.

Further reductions in environmental releases from pulp mill waste outfalls may result from improving the control of suspended solids in the secondary waste treatment plant. TCDD and TCDF are relatively insoluble in water, but they adhere tightly to fine colloidal material and suspended solids. A well-designed, properly operated secondary treatment plant is capable of removing up to 90 percent of the TCDD and TCDF released. Dioxins are retained in treatment plant sludge. The sludge is normally disposed of in landfills, where limited studies show that it remains isolated and immobile. Some sludge is retained in sludge lagoons or is incinerated, but a portion is used for soil conditioners. The remaining 10 percent of the dioxin that remains in suspension can find its way in to the water coarse and remain as sediment in streambeds. The use of clarifiers, chemicals, and settling basins to improve the efficiency of waste treatment, coupled with chlorine dioxide substitution and/or perhaps other delignification technology might prove to be the optimum solution for some existing pulp mills.

More questions remain than do answers as to what risk dioxin from pulp and paper manufacture presents to humans and the environment: will additional regulations be needed to reduce the risk of human exposure from dioxin and other chlorinated compounds produced in pulp mills? and which technologies or mix of technologies are best suited for reducing the production of dioxin in the pulp bleaching process? The pulp and paper industry has a number of technical options available to meet the problem. Other technologies, such as extended delignification and the substitution of other oxidants in the bleach process for chlorine gas, may be as effective as oxygen delignification in reducing the use of chlorine. All of these questions require more detailed study before they can be answered with acceptable certainty. Final decisions to meet regulatory requirements will have to be made on a case-by-case, mill-by-mill basis.