UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF WATER

MAY 21 1990

MEMORANDUM

SUBJECT: **Strategy for the Regulation of Discharges of PHDDs and PHDFs from Pulp and Paper Mills to Waters of the United States**

FROM: LaJuana S. Wilcher
Assistant Administrator

TO: Regional Water Management Division Directors
NPDES State Directors

The "Strategy for the Regulation of Discharges of PHDDs and PHDFs from Pulp and Paper Mills to the Waters of the United States" is attached. (For this strategy PHDD and PHDF refer to the family of compounds called polyhalogenated dibenzo-p-dioxins and dibenzofurans, respectively.) The purpose of this strategy is to update information which was included in EPA's "Interim Strategy for the Regulation of Pulp and Paper Mill Dioxin Discharges to the Waters of the United States" (August 9, 1988) and to provide additional guidance on several aspects of assessment and control of discharges of PHDDs, PHDFs, and other chlorinated organics from chlorine bleaching pulp and paper mills.

This strategy is designed to be EPA's recommended approach, based on current information, to the regulation of discharges of PHDDs and PHDFs from chlorine bleaching pulp and paper mills to waters of the United States. As such, it relies on all applicable CWA authorities including, but not limited to, Section 304(l). The strategy is also intended to fulfill the Agency's obligations under paragraph 19 of the Consent Decree in Environmental Defense Fund and National Wildlife Federation vs. Thomas, No. 85 - 0973. Due to its comprehensive nature, the strategy provides information and recommendations in a number of areas not covered by the terms of the Consent Decree.

The Office of Water (OW) has issued regulations and several guidance documents which are relevant to the regulation of effluent discharges from U.S. pulp and paper mills. These documents are listed and summarized in the attached strategy.

Copies of all final documents are available from EPA Headquarters (Office of Water Regulations and Standards and Office of Water Enforcement and Permits).

In addition to the various guidance documents, several initiatives are currently underway and are summarized in the attached strategy. Data from the 104 Mill Study are presently being evaluated and a final report is expected in the near future. A summary of technologies for the control and reduction of chlorinated organics was sent to EPA Regions and States on May 8, 1990. The preliminary report of the Bioaccumulation Study was sent to the EPA Regional Bioaccumulation Study Coordinators and a final report is expected by the end of the fiscal year. Finally, EPA's analytical method 1613 has been developed and preliminary results from the interlaboratory comparability study are expected in the near future. (The interlaboratory evaluation is scheduled to begin in May 1990.) Although this method has not yet been formally promulgated, its use is recommended. Information on any of these projects may be obtained by contacting the Office of Water Regulations and Standards.

Knowledge on various state-of-the-art production processes and their ability to reduce the production and discharge of PHDDs, PHDFs, and other toxic organic compounds is increasing rapidly and should be considered in establishing limitations on the discharge of such compounds from a facility. We have provided and are continuing to provide assistance to EPA Regions and States in evaluating performance of these technologies and processes and developing permit limitations.

The attached strategy summarizes specific requirements for permits developed under Section 304(l) as well as for those permits issued under authorities other than Section 304(l). The strategy emphasizes that in all cases, final effluent limits must include the more stringent of either technology-based or water quality-based permit limitations as required by the Clean Water Act.

The fundamental approach presented in EPA's March 15, 1989 guidance entitled, "Final Guidance on Section 304(l) Listing and Permitting of Pulp and Paper Mills" is not changed by this strategy. Permits issued following the principles of the March 15, 1989 guidance will comply with the principles of this strategy. However, this strategy provides additional clarification concerning the recommended analytical method for 2,3,7,8-TCDD and the associated detection level. Information is also provided in this strategy concerning recommended monitoring approaches for situations where the calculated water quality-based limits are below the detection level. These approaches include internal waste stream monitoring/limitation points;

monitoring for PHDFs and applying a plant-specific PHDD/PHDF ratio to project 2,3,7,8-TCDD concentrations; and fish tissue collection and analyses.

The attached strategy is guidance; it is a general statement of policy. It does not establish or affect legal rights or obligations. It does not establish a binding norm and is not finally determinative of the issues addressed. Agency decisions in any particular case will be made applying the law and regulations on the basis of specific facts and actual action.

In some cases, this strategy reiterates statutory or regulatory requirements, and cites to the relevant statutory or regulatory provisions. Otherwise, the strategy makes recommendations only; these recommendations are not accompanied by statutory or regulatory cites.

If you would like to discuss this strategy, please feel free to call Jim Elder (FTS/202-475-8488) if you have questions on NPDES permitting; or call Martha Prothro (FTS/202-382-5400) with questions on water quality standards, analytical studies or evaluation of technology.

Attachments

cc: Environmental Services Division Directors
Water Quality Branch Chiefs
Permits Branch Chiefs
Charles Elkins (TS-792)
Susan G. Lepow (LE-132W)
Mahesh Podar (PM-221)

STRATEGY FOR THE REGULATION OF DISCHARGES OF PHDDS AND PHDFS FROM PULP AND PAPER MILLS TO WATERS OF THE UNITED STATES

EPA's goal is to reduce the amount of chlorinated organics and eliminate the presence of polyhalogenated dibenzo-p-dioxins and dibenzofurans (PHDDs and PHDFs) in discharges from pulp and paper mills to the waters of the United States. This goal should be reflected in National Pollutant Discharge Elimination System (NPDES) permits based on technology-based requirements (using best professional judgment), future national technology-based effluent guidelines, and/or on State water quality standards designed to protect aquatic life and human health.

Chlorine bleaching pulp and paper mills are known to discharge chlorinated organic compounds as a by-product of the chlorine bleaching process. Contained in this large family of compounds are polyhalogenated dibenzo-p-dioxins (PHDDS) and polyhalogenated dibenzofurans (PHDFs). PHDDs and PHDFs are a family of chlorinated aromatic organic compounds which are structurally and chemically related. Two specific PHDD and PHDF compounds of particular concern due to their high toxicity are 2,3,7,8-TCDD and 2,3,7,8-TCDF.

The Office of Water (OW) has issued regulations and several guidance documents regarding the regulation of dioxin discharges from U.S. pulp and paper mills. The documents issued to date and a brief summary of the contents of each is as follows:

- **"Interim Strategy for the Regulation of Pulp and Paper Mill Dioxin Discharges to the Waters of the United States" (8/9/88):** Four important objectives for interim regulation of dioxin discharges from pulp and paper mills are discussed, including recommendations on how to accomplish these tasks and a description of available mill or fish data. The recommendations were designed to be applied immediately, pending the outcome of various studies and regulatory initiatives. The attachments to the August 9, 1988 interim guidance are still current; however, new information as it becomes available will be distributed by the Office of Water Enforcement and Permits (OWEP) to EPA Regions and States.

- **"Release of Dioxin Treatability Study and Interim Control Measures for Regulating Dioxin Discharges from Pulp and Paper Mills" (10/20/88):** This document reported the preliminary results of EPA's bench scale wastewater treatability study for 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) in pulp and paper mill wastewaters. The study also outlined interim control measures consistent with the August 1988 strategy.

- **"Final Guidance on Section 304(l) Listing and Permitting of Pulp and Paper Mills" (3/15/89):** This guidance recommended approaches for regulating pulp and paper mills identified as impacting waters of the U.S. listed under Section 304(l), including specific requirements for individual control strategies (ICS) and associated statutory deadlines.

- **"Surface Water Toxics Control Regulation (54 - Federal Register 23868" (6/2/89)):** This regulation and the associated preamble interpret the specific statutory requirements of Section 304(l) of the Clean Water Act. In addition, they clarify EPA's surface water toxics control regulations and provide a greater level of specificity than previously existed in regulation.

- **"Pulp and Paper/Dioxin Strategy Team - Transmittal of Information on Technology, Analytical Methods, and Bioaccumulation Study" (12/14/89):** This document provided all of the latest available information as of December 1989 to permit writers to assist them in developing ICS's under Section 304(l). The document included preliminary data on the 104 mill Study, a summary of EPA analytical method 1613, and copies of permits issued to Section 304(l) listed pulp mills. It also reported on other areas such as the Bioaccumulation Study and the latest improvements in mill technologies for dioxin reduction.

- **"State Policies, Water Quality Standards, and Permit Limitations Related to 2,3,7,8-TCDD in Surface Water" (1/5/90):** This memorandum addressed the degree of flexibility available to States in establishing policies, standards, and permit limits related to 2,3,7,8-TCDD. The document's purpose was to clarify EPA's general policy on this matter and the circumstances under which EPA Regions should approve or deny State decisions on water quality standards for dioxin, including recent adoptions of numeric water quality standards by the State.

The underlying principles contained in both the first and third listed guidance documents above (dated 8/9/88 and 3/15/89) are reasserted by today's strategy. A more detailed discussion of these underlying principles as well as additional considerations appears below under "Issuance of NPDES Permits." The March 15, 1989 guidance made a number of specific recommendations concerning the listing of waters and facilities and the development of ICSs for chlorine bleaching pulp and paper mills under Section 304(l) of the CWA. Today's strategy reiterates those recommendations and supplements them by providing additional requirements and recommendations for the development of NPDES permits for chlorine bleaching pulp and paper mills. Today's strategy should therefore be used by permitting authorities as the Agency's guidance for the

development of NPDES permits for chlorine bleaching pulp and paper mills. The guidance contained in the January 5, 1990 memorandum is unchanged by this strategy. Regulatory authorities should utilize the most current information available when making regulatory decisions, which may consist of information contained in these earlier memoranda as well as more recent data referenced in this strategy.

This strategy calls for: (1) aggressive action to fully implement or, where necessary, develop State water quality standards for 2,3,7,8-TCDD at all sites where mills using chlorine bleach processes are discharging; (2) collection of new data on pulps, effluents and sludges from mills in which the level of 2,3,7,8-TCDD is uncertain or undetectable because it is below the detection limit (either as part of NPDES permit application or as permit special conditions); (3) detailed technical evaluation of in-process changes and/or wastewater treatment technologies to reduce the presence of chlorinated organics including PHDDs and PHDFs in wastewater discharges; and (4) issuance of NPDES permits that regulate and require monitoring for chlorinated organics including PHDDs and PHDFs, examine effluent toxicity, and provide for modification to tighten controls consistent with this strategy and the requirements of the Clean Water Act (CWA).

This strategy is designed to be EPA's recommended approach, based on current information, to the regulation of discharges of PHDDs and PHDFs from chlorine bleaching pulp and paper mills to waters of the United States. As such, it relies on all applicable CWA authorities including, but not limited to, Section 304(l). The strategy also begins to address other chlorinated organics.

In addition, this strategy is guidance; it is a general statement of policy. It does not establish or affect legal rights or obligations. It does not establish a binding norm and is not finally determinative of the issues addressed. Agency decisions in any particular case will be made by applying the law and regulations on the basis of specific facts and actual action.

In some cases, this guidance reiterates statutory or regulatory requirements, and cites to the relevant statutory or regulatory provisions. Otherwise, the strategy makes recommendations only; these recommendations are not accompanied by statutory or regulatory cites.

WATER QUALITY STANDARDS DEVELOPMENT

As of March 1990, a total of 45 out of 57 States and territories had 2,3,7,8-TCDD human health criteria adopted, proposed or expected to be proposed. Of the 45, 21 States and territories have promulgated numeric human health criteria or

translator procedures for 2,3,7,8-TCDD. Ten States have proposals to adopt numeric human health criteria or translator procedures for 2,3,7,8-TCDD with most of these scheduled for adoption by the end of FY 90. Fourteen States are expected to adopt numeric human health criteria or translator procedures but have not yet issued formal proposals. In 1984, EPA issued a water quality criteria guidance document for 2,3,7,8-TCDD pursuant to Section 304(a) of the CWA and established EPA methodologies. States have the authority to establish standards for other pollutants beyond 2,3,7,8-TCDD in accordance with Agency guidance.

In accordance with the requirements of CWA Section 303(c)(2)(B), the Regions need to continue to assure that all States with waters affected by pulp and paper mill discharges develop an appropriate numeric water quality criterion for 2,3,7,8-TCDD for those waters as quickly as possible. The criterion can be based upon the existing EPA criteria document for 2,3,7,8-TCDD, and any additional data and/or site-specific conditions. In all cases, the necessary steps for the adoption of numeric water quality criteria (or derived numeric criteria) for 2,3,7,8-TCDD should continue to move rapidly to completion. Such steps include completion of any necessary exposure assessments, State selection of its preferred risk level, compilation of appropriate monitoring data, and public participation.

A list of documents which can be used to assist in adopting a 2,3,7,8-TCDD criterion, including development of site-specific risk assessments, was included as an attachment in the August 9, 1988 interim guidance entitled, "Interim Strategy for the Regulation of Pulp and Paper Mill Dioxin Discharges to the Waters of the United States." Also, the January 5, 1990 memorandum, entitled "State Policies, Water Quality Standards, and Permit Limitations Related to 2,3,7,8-TCDD in Surface Water", provides answers to questions concerning the degree of flexibility available to States in establishing policies and standards related to 2,3,7,8-TCDD. That document clarified EPA's general policy and the circumstances under which EPA Regions should approve or deny State decisions that differ from EPA's approach. The Office of Water will continue to provide assistance to Regions and States in specific cases.

NATIONAL DATA COLLECTION ACTIVITIES

EPA is now completing its reports on data from the National Bioaccumulation Study and the EPA/Paper Industry Cooperative Dioxin Study (104 Mill Study). When completed, copies of the results of these studies may be obtained by contacting the

Assessment and Watershed Protection Division and the Industrial Technology Division, respectively, within the Office of Water Regulations and Standards, at U.S. EPA Headquarters.

As part of the National Bioaccumulation Study, EPA analyzed for PHDDs and PHDFs in fish which were collected near chlorine bleaching pulp and paper mills. Fish tissue data from areas near these mills were distributed to the Regions according to the procedures established in February 1988. The final Bioaccumulation Study report is expected by the Fall of 1990.

The EPA/Paper Industry Cooperative Dioxin Study was signed by all parties on April 25, 1988. As a result of this study, EPA received dioxin data from 104 pulp mills that bleach chemical pulps, including process information and dioxin analyses on effluent, sludge, and pulp from all 104 mills. EPA Headquarters staff provided preliminary data to the Regions as it became available; the latest data summary was provided on December 14, 1989. A preliminary report on the evaluation of the data is expected in the near future, at which time it will be distributed to the Regions and States.

EPA method number 1613 has been revised and updated. Although the method has not yet been formally promulgated under 40 CFR Part 136, it is recommended for use in conjunction with permit limitations for all dioxin and furan congeners. Method 1613 is a high resolution capillary column gas chromatography (HRGC)/high resolution mass spectrometry (HRMS) method for analysis of tetra-through octa- chlorinated dibenzo-p-dioxins and dibenzofurans using isotope dilution. Method 1613 was developed by the Industrial Technology Division in the Office of Water (ITD) to provide improved precision and accuracy of analysis of pollutants in aqueous and solid matrices. A brief summary of method 1613 prepared by ITD is attached (Attachment 1).

As a part of the analytical method promulgation process, EPA staff are continuing to work on further validation of EPA method 1613 for dioxins in pulp mill matrices. The interlaboratory evaluation of method 1613 is scheduled to begin in May, 1990. At least ten laboratories from five countries have agreed to participate in the study. Data from the study will be used by the Agency to provide the basis for constructing estimates of precision and accuracy, estimates of inter- and intralaboratory components of variability for the method, and to generate improved method specifications. In addition, EPA anticipates this study will result in expansion of the number of labs with demonstrated capability to perform method 1613 analyses. EPA method 1613 will be proposed as an approved method under 40 CFR Part 136 in the near future.

In addition, ITD is currently reviewing both the "International Standards Organization" (ISO/DIS 9562) analytical method and Scan W-9:89 method for Adsorbable Organic Halogens (AOX). ITD plans to proceed with a proposal of an equivalent U.S. EPA approved AOX method for eventual promulgation as a final method in the near future.

TECHNICAL EVALUATION OF WASTEWATER TREATMENT TECHNOLOGIES AND/OR IN-PROCESS CHANGES TO REDUCE OR ELIMINATE PHDD/PHDF DISCHARGES

EPA has initiated a program to revise the existing pulp and paper effluent limitations guidelines regulation, with a view toward establishing limitations for PHDDs, PHDFs, other chlorinated organics, and other nonconventional and toxic pollutants of concern based on the best available technology economically achievable (BAT). As a part of this activity, EPA is evaluating the effectiveness of various process modifications, such as oxygen delignification and chlorine dioxide bleaching, in reducing the generation and discharge of PHDDs, PHDFs and other chlorinated organics.

Evaluation of numerous in-plant processes and wastewater treatment systems and an extensive literature search is discussed in an EPA report entitled, "Summary of Technologies for the Control and Reduction of Chlorinated Organics from the Bleached Chemical Pulping Subcategories of the Pulp and Paper Industry." This report was distributed to Regions and States on May 8, 1990.

As a part of the Cooperative Dioxin Study, the paper industry agreed to conduct a more intensive study of twenty-five bleaching lines. This study included detailed process evaluation at mills that use a variety of bleaching processes. The objectives of the study included determination of the bleaching operations in which dioxin is formed, process conditions affecting dioxin formation, and factors affecting dioxin removal from the bleaching process. As of this date, the results of this study have not been provided to the Agency. When this information becomes available it will be provided to the Regions and States.

EPA conducted a treatability study at two bleached kraft facilities to evaluate total suspended solids (TSS) and 2,3,7,8-TCDD and 2,3,7,8-TCDF reduction resulting from coagulant and polymer addition. The results from the analyses for these first two bleached kraft facilities have been provided to EPA Regions. This effort has been expanded within EPA to include further research by EPA's Office of Research and Development (ORD). The study is scheduled for completion by late 1990.

EPA staff is continuing to collect and seek the latest information from other governments, particularly Sweden and Canada, concerning regulation development, effluent data, and

available state-of-the-art technologies. This information will continue to be made available to the Regions and States by EPA Headquarters, as appropriate.

ISSUANCE OF NPDES PERMITS

There are certain statutory and regulatory requirements applicable to all chlorine bleaching pulp and paper mill discharges. Special considerations appropriate for each type of permit are discussed separately below, followed by consideration of various permit strategies and elements which should be considered for any permit for a chlorine bleaching pulp and paper mill. "Individual control strategies" (ICSs) pursuant to Section 304(l) of the CWA are required for some, but not all, chlorine bleaching pulp and paper mill discharges.

Permits Developed under Section 304(l) of the CWA

All chlorine bleaching pulp and paper permits that also constitute ICSs pursuant to Section 304(l) of the CWA for 2,3,7,8-TCDD, should be developed in accordance with EPA's surface water toxics control regulation (June 2, 1989, FR Vol. 54 No. 105 p.23868) and the March 15, 1989 guidance, entitled "Final Guidance on Section 304(l) Listing and Permitting of Pulp and Paper Mills." In accordance with the requirements at 40 CFR Part 122.44(d)(1), these pulp and paper permits must contain specific water quality-based limitations for 2,3,7,8-TCDD that the regulatory authority determines to be necessary to ensure compliance with a State numeric water quality criterion for 2,3,7,8-TCDD or the State's narrative criterion for toxicity. The permits must also require compliance with these effluent limitations as soon as possible, but in no case later than the statutory deadlines required by Section 304(l)(1)(D). (Compliance with these deadlines must be 3 years after establishment of the ICS; in most cases these deadlines should be on or about June 4, 1992, for ICSs approved in June 1989 by EPA and June 4, 1993, for ICSs which were originally disapproved by EPA in June 1989.)

All ICSs which were approved on June 4, 1989 as draft permits were to have been issued as final permits by February 4, 1990. ICSs which were disapproved on June 4, 1989 should be draft or final permits subject to EPA approval by June 4, 1990. On June 4, 1989, 91 pulp and paper mills and 5 Publicly Owned Treatment Works (POTWs) receiving discharges from mills were identified as requiring ICSs because of their 2,3,7,8-TCDD impacts to receiving waters. This list of facilities requiring ICSs has subsequently been revised as a result of the public comment period. A number of facilities have been deleted, primarily based on determinations by EPA that the waters to which they discharge are no longer listed on the "short" list of impaired waters (pursuant to CWA Section 304(l)(1)(B), a list of

those waters which, after application of technology-based effluent limits, the State does not expect will achieve applicable water quality standards, due entirely or substantially to point source discharges of priority pollutants). Some facilities have also been added. Such decisions may be based on new information, including that provided in public comments, which has become available since the initial decisions were made. However, as noted below (under "Permit Limits Developed under other CWA Authorities"), facilities which are deleted from the Section 304(l) lists will still be required to meet all applicable CWA requirements during normal permit reissuance or modification processes.

All permits (both 304(l) and non-304(l)) which expire and are reissued should be comprehensive permits in all other respects in addition to containing limitations on 2,3,7,8-TCDD where necessary. Appropriate limitations and monitoring conditions for all parameters for which water quality-based or technology-based limitations are required must be included in permits in accordance with the requirements of the CWA at Section 301(b)(1) and (2). In particular, these permits should contain technology-based limits where such limitations are more stringent than those based on attaining water quality standards.

These permits should also include any appropriate conditions concerning the investigation of interim control measures, and other conditions, if any, necessary to assure compliance with permit limitations and requirements (see discussion below of interim control measures and additional conditions set pursuant to CWA Section 402(a)).

All water quality-based limitations (in both 304(l) ICSs and in non-304(l) permits) should be developed in accordance with sound scientific principles and should properly account for all relevant site-specific considerations. EPA has provided a number of guidance documents for regulatory authorities on the various aspects of this process, including the "Technical Support Document for Water Quality-based Toxics Control" (September 1985). Specific elements which need to be adequately considered include the duration and frequency requirements of the water quality criterion, the critical receiving water flows, selection of water quality models, information on all sources of pollutants of concern, and translation of wasteload allocation requirements into enforceable permit limitations.

Determinations of critical receiving water flows and any applicable mixing zones are at the discretion of the State regulatory authority subject to review by EPA. However, where unsafe fish tissue levels or other evidence indicates that a bioaccumulative pollutant is being incorporated into the aquatic organisms, special care should be taken in determining the

appropriateness of mixing zones and subsequent development of permit limitations. EPA's mixing zone policy is described in more detail in its "Water Quality Standards Handbook" (1984).

March 15, 1989 Guidance

The March 15, 1989 guidance made a number of recommendations and reiterated a number of statutory requirements concerning the identification of waters, as well as sources and amounts of pollutants, under CWA Section 304(l). The March 15, 1989 guidance on listing under Section 304(l) remains current and in effect.

The March 15, 1989 guidance also made a number of specific recommendations concerning the development of ICSs for chlorine bleaching pulp and paper mills under Section 304(l) of the CWA. Today's strategy reiterates those recommendations and supplements them by providing additional requirements and recommendations for the development of NPDES permits for chlorine bleaching pulp and paper mills. Today's strategy should therefore be used by permitting authorities as the Agency's guidance for the development of NPDES permits for chlorine bleaching pulp and paper mills. Current permits based on the March 15, 1989 guidance are consistent with the principles described here.

The March 15, 1989 guidance indicated that water quality-based limits for 2,3,7,8-TCDD derived to protect a numeric criterion in a State water quality standard for 2,3,7,8-TCDD or a numeric interpretation of a narrative criterion in a State water quality standard should be placed in NPDES permits. On June 2, 1989, when EPA amended its regulations at 40 CFR Part 122.44(d)(1) (54 FR 23868, 6/2/89), this recommendation became a requirement. The regulations at 40 CFR 122.44(d)(1) require all NPDES permits to include, where necessary, limitations to control all pollutants or pollutant parameters which the Director (permitting authority) determines may be discharged at a level which will cause, have the reasonable potential to cause, or contribute to an excursion above any State water quality standard, including State narrative criteria for water quality.

EPA is hereby reaffirming the following fundamental principles contained in the March 15, 1989 guidance (and supported by the regulations at 40 CFR Part 122.44(d)(1)) with regard to ICSs under CWA Section 304(l) and other non-304(l) permits that require water quality-based effluent limitations (note section 304(l) applies to section 307(a) toxic pollutants, which include 2,3,7,8-TCDD):

- Where a water quality-based limit on 2,3,7,8-TCDD is necessary in the permit, that limit should be established using the State's adopted numeric criterion for 2,3,7,8-TCDD or where the State has not adopted a numeric criterion

for 2,3,7,8-TCDD in its water quality standards, using one of three options (in accordance with 40 CFR 122.44 (d)(1)(vi):

(1) using a calculated numeric water quality criterion for 2,3,7,8-TCDD based on a proposed State criterion, or an explicit State policy or regulation interpreting its narrative water quality criterion;

(2) using EPA's water quality criterion for 2,3,7,8-TCDD on a case-by-case basis; or

(3) establishing effluent limitations on an indicator parameter for 2,3,7,8-TCDD (subject to the provisions of 122.44(d)(1)(vi)).

- In addition, permits should contain BPJ/BAT effluent limitations pursuant to Sections 402(a)(1) and 304(b) of the CWA and regulations at 40 CFR Part 125.3 for 2,3,7,8-TCDD for each facility, thereby establishing an appropriate technology-based limitation before the 1992 (or 1993) compliance date for compliance with the water quality-based limit. These limits will be the controls which are currently imposed on the mills and move the mills towards compliance with the more stringent water quality-based limit.

- An EPA-approved ICS must require compliance with the final water quality-based effluent limitations in the ICS as soon as possible, but in no case later than three years after establishment of the ICS (in most cases compliance should be no later than June 4, 1992). An ICS that was originally disapproved by EPA and subsequently developed by EPA in cooperation with the State or by the State based on agreements with EPA, must also require compliance with the final water quality-based effluent limitations in the ICS as soon as possible, but in no case later than three years after establishment of the ICS (in most cases compliance should be no later than June 4, 1993). (See Clean Water Act Section 304(1)(1)(D).)

- The permits must contain limitations as necessary to meet State water quality standards (see CWA Section 301(b)(1)(C)). Where the final calculated effluent limitation for 2,3,7,8-TCDD is below the current level of detection, EPA recommends that the permit contain the calculated water quality-based limit for 2,3,7,8-TCDD and necessary effluent monitoring for 2,3,7,8-TCDD. The permit should also contain:

1. A statement that the detection level is the threshold for compliance/non-compliance determinations (the term "detection level" is defined in detail under the section below entitled "Dioxin Analytical Methods and Detection Levels").

2. A statement citing the analytical protocol to use when analyzing the effluent for 2,3,7,8-TCDD. The March 15, 1989 guidance recommended the analytical protocol set out in Appendix C of USEPA/Paper Industry Cooperative Dioxin Screening Study (EPA 440/1-88-025, March 1988). Today's strategy recommends an analytical method that is an updated version of the one specified in the March 15, 1989 guidance (see the discussion below on "Dioxin Analytical Methods and Detection Levels").

The above guidance should be supplemented by the recommendations below under the heading, "Recommendations for Specific Permit Elements."

Permit Limits Developed Under Other CWA Authorities

For mills which do not require an ICS under Section 304(l), permits must still include the more stringent of either technology-based or water quality-based limitations on all pollutants or pollutant parameters of concern in accordance with requirements of Sections 301(b)(1) and (2) of the CWA. All permits should be reissued upon expiration and include all appropriate requirements as discussed above. In addition, prior to reissuance, permits should be reopened and modified where appropriate in accordance with the provisions of 40 CFR Part 122.62(a) (Note that the permitting authority may only review the specific permit terms for which the grounds for modification exist.) In some cases, it may be necessary to revoke and reissue the permit prior to its expiration date if one or more of the conditions for permit revocation under 40 CFR 122.62(b) is met.

Technology-based Requirements

Permits for all mills that bleach with chlorine or chlorine derivatives should either be reissued upon expiration or prior to reissuance, reopened and modified to establish an appropriate BPJ/BAT effluent limitation for PHDDs, PHDFs and other pollutants of concern for the mill. Reopening and modifying of permits should be in accordance with the provisions of 40 CFR Part 122.62(a). The methodology used for developing a BPJ/BAT limitation should be consistent with EPA's regulations at 40 CFR 125.3(d) as outlined in the "Training Manual for NPDES Permit Writers (May 1987)."

Development of BPJ/BAT effluent limitations should be based on an evaluation of in-plant control processes and wastewater treatment facilities. In-plant controls can include various methodologies designed to reduce formation of PHDDs, PHDFs, and other chlorinated organics in pulping and bleaching operations.

Reductions in discharges of these compounds can also be achieved by optimizing suspended solids controls, particularly from secondary clarifiers or lagoons at biological treatment facilities.

The results of the various national data collection activities discussed earlier should be reviewed. The results of the treatability study may be useful in developing these limitations. The Cooperative Dioxin Study provided dioxin data from effluents, pulps, and sludges from 104 mills that bleach chemical pulps with chlorine or chlorine derivatives. These data were made available to the Regions and States and may be helpful in modifying or developing the permit requirements to reflect the significance of the discharges. However, more recent data may exist for many of these mills and should be obtained where available.

The permitting authority should also consider including conditions that would require the permittee to investigate and report on the use of additional short-term control measures. The authority for such conditions is provided by Sections 402(a)(2) and 308(a) of the CWA. The primary objective of such conditions would be for the permittee to report to the regulatory authority on those measures it plans to implement to achieve compliance with permit limitations and, if appropriate, to investigate the feasibility of certain other control measures. Such measures (e.g., chlorine substitution) can lead to the prevention of pollutant formation and resultant environmental benefit.

The results of such a program could be used to reopen a permit to revise BPJ/BAT limitations if necessary or to establish such limitations where not yet in place. In addition, following this study of control measures, the permitting authority, under CWA Section 402(a)(2), may want to set such further conditions in the permit as are necessary to assure compliance with permit limitations and requirements. Where such control measures are being assessed as possible technology-based limitations, cost may be considered in accordance with 40 CFR 125.3(d). A control measure study of this type would typically be required in conjunction with BPJ/BAT technology-based limitations. An example control measure program is attached (Attachment 2).

The statutory deadline for compliance with all technology-based requirements of the CWA was March 31, 1989. Thus, compliance with technology-based effluent limitations must be required upon the effective date of the permit. Where such

limitations cannot be met immediately, administrative orders should be issued with schedules requiring compliance as soon as possible, as determined by the permitting authority.

Water Quality-based Requirements

Water quality-based requirements must be developed in accordance with the requirements of 40 CFR 122.44(d) and should conform with the recommendations discussed above from the March 15, 1989 guidance. Permits not specifically covered under Section 304(l) because the criteria for listing the water and facility under Section 304(l) were not met, may still require water quality-based limitations on 2,3,7,8-TCDD as well as other PHDDs and PHDFs. This may include situations where information that indicated a need for such limits was not available at the time that Section 304(l) lists of impaired waters and responsible point sources was compiled, but has subsequently become available (e.g., as a result of permit monitoring requirements or monitoring required by the permit application). Where information is not available to determine whether water quality-based limitations are needed, reissued permits should contain special monitoring requirements (as discussed below) together with specific reopener requirements that could lead to modifying the existing limitations, if necessary, based upon the results of the monitoring.

It is also important to establish water quality based effluent limitations, where appropriate, on discharges of chlorinated organics from publicly owned treatment works (POTWs) which receive discharges from chlorine bleaching pulp and paper mills. Such limits will provide a strong regulatory and technical basis for requiring local limits, where appropriate, on chlorine bleaching pulp and paper mills which are industrial users of POTWs, in order to prevent pass through and interference.

Water quality-based limitations for 2,3,7,8-TCDF should also be developed where appropriate. EPA has not yet developed a Section 304(a) water quality criterion guidance document for 2,3,7,8-TCDF, nor have many States adopted a criterion for 2,3,7,8-TCDF as part of their water quality standards. It may therefore be scientifically difficult to establish water quality-based permit limits for 2,3,7,8-TCDF. Nevertheless, permitting authorities may establish water quality-based permit limitations for furans based on an applicable State narrative criterion and in accordance with Section 301(b)(1)(C) of the CWA.

It is also expected that reductions in PHDDs in accordance with limitations on 2,3,7,8-TCDD can be expected to result in some concomitant removals of PHDFs (see additional discussion

below). EPA will be investigating the extent to which ancillary removals of other compounds can be expected to occur as a result of 2,3,7,8-TCDD reductions. At a minimum, EPA recommends that PHDD and PHDF monitoring as well as some of the additional monitoring tools discussed below be included in permits pursuant to Section 402(a) of the CWA.

Compliance with such water quality-based limitations should be in accordance with the following provisions. Dischargers must comply with water quality-based limits on the effective date of the permit unless a schedule of compliance is authorized pursuant to the applicable State water quality standards or regulations implementing the standards (see Decision of the Administrator, in the Matter of Star-Kist Caribe, Inc., NPDES Permit 88-5, April 11, 1990.)

RECOMMENDATIONS FOR SPECIFIC PERMIT ELEMENTS

The following discussion applies to any permit developed for chlorine bleaching pulp and paper mills, whether or not such a permit is required under Section 304(l) authorities.

Limitations or Monitoring Requirements on Key Parameters

Whole Effluent Toxicity

Permits are to include limitations on whole effluent toxicity and associated monitoring requirements as necessary to achieve any applicable State water quality standard (see 40 CFR 122.44(d)(1)(iv) and (v)).

Limitations on whole effluent toxicity are intended to protect against acute and chronic toxic effects on aquatic life of a whole effluent mixture. Limits on whole effluent toxicity at chlorine bleaching pulp and paper mills, while not necessarily protective of human health, may be necessary to help address the overall toxicity of the discharge caused by complex mixtures of chlorinated organics. Such complex mixtures at chlorine bleaching pulp and paper mills are expected to contain levels of PHDDs and PHDFs. Limits on whole effluent toxicity will therefore help ensure that PHDDs and PHDFs are appropriately addressed (with respect to effects on aquatic toxicity) where numerical water quality-based limitations for PHDDS and PHDFs have not yet been established. Where toxicity monitoring data do not exist, toxicity monitoring should be required together with a reopener to establish limitations where necessary.

Requirements for a toxicity reduction evaluation (TRE) should also be included, where appropriate, as described below. Where monitoring data indicate unacceptable effluent toxicity, the TRE is the principal mechanism for investigating causes of toxicity and steps necessary to bring the discharge into

compliance with a water quality-based whole effluent toxicity effluent limitations. The purpose of a TRE is to provide the discharger with the opportunity to investigate the causes of and identify corrective actions for difficult effluent toxicity problems.

Chlorinated Organics

Adsorbable Organic Halogens (AOX)

2,3,7,8-TCDD is only one of a number of toxic chlorinated organic compounds in chlorine bleached effluents, many of which have yet to be identified. The use of surrogate parameters, indicative of levels of chlorinated organics, can provide valuable monitoring information.

Numerous methods have been developed for the measurement of chlorinated organics, including Total Organic Chlorine (TOCl), Adsorbable Organic Halogens (AOX), Total Organic Halogens (TOX) and Extractable Organic Halogens (EOX). Of these parameters, EPA's current information indicates that the most effective choice for monitoring is AOX. The advantages of monitoring for AOX are as follows: (1) analysis is rapid and not difficult to perform; (2) cost of the analysis is relatively inexpensive (approximately $125/sample); (3) good repeatability associated with test results, and (4) good data comparability due to an already existing and rapidly expanding database. For these reasons, EPA currently believes that AOX is the best choice for a surrogate measure of total chlorinated organics and strongly encourages permit writers to include AOX as a monitoring requirement in permits pursuant to Section 402(a) of the CWA. Additional information concerning AOX and the AOX analytical methods (ISO/DIS 9562) and Scan W-9:89 appear in Attachment 3.

As previously stated, ITD is currently reviewing both the "International Standards Organization" (ISO/DIS 9562) analytical method and Scan W-9:89 method for Adsorbable Organic Halogens (AOX). ITD plans to proceed with a proposal of an equivalent U.S. EPA approved AOX method for eventual promulgation as a final method in the near future.

Toxicity Equivalents Approach (TEQ)

The Toxicity Equivalents (TEQ) approach used with respect to PHDDs and other chlorinated organics was first presented in a memorandum from U.S. EPA Administrator Thomas on January 7, 1987, which recommended the use of the 1987 "Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-dioxins and Dibenzofurans (CDDs and CDFs)" (EPA/625/3-87/012). This report was recently updated and republished in 1989 under the same title (EPA/625/3-89/016) to include the latest data and research on the TEQ approach. The

current Administrator has also recommended use of this 1989 report for the Agency wherever regulatory activities are involved.

An assessment of the human health risk of a mixture of PHDDs and PHDFs, using the TEQ approach, involves the following steps:

(1) Analytical determination of the PHDDs and PHDFs in the sample using U.S. EPA method 1613.

(2) Multiplication of congener concentrations in the sample by the toxicity equivalent factor (TEF) in Attachment 4 to express the concentration in terms of 2,3,7,8-TCDD equivalents.

(3) Summation of the products in step 2 to obtain the total 2,3,7,8-TCDD equivalents in the sample.

Attachment 4 lists a TEF for each of the respective congeners including 2,3,7,8-TCDD which is set at a TEF of 1, since it is considered to be the most potent of the congeners. There are a total of 210 congeners of dioxin and furan, including 2,3,7,8-TCDD. All of the remaining congeners are set at some proportional fraction of potency (less than one) with respect to the potency of 2,3,7,8-TCDD. For example, 2,3,7,8-TCDF has a TEF of 0.1 which means that it is considered 1/10th as potent as 2,3,7,8-TCDD. Therefore, if a permit required monitoring for both 2,3,7,8-TCDD and 2,3,7,8-TCDF and a monitoring sample reflected concentrations of 10 ppq 2,3,7,8-TCDD and 5 ppq 2,3,7,8-TCDF then the total TEQ for this sample would be 10.5 ppq TEQ. TEQ data may be used to determine the amount of other chlorinated compounds, such as 2,3,7,8-TCDF, contributing to the overall toxic effect of the permittee's discharge.

In order to assess and limit, as appropriate, the various dioxin and furan congeners, at this time, EPA recommends monitoring and, where the permitting authority has sufficient site-specific information, limits on PHDDs and PHDFs expressed in terms of Toxicity Equivalents (TEQ). TEQ should be calculated using the three steps described above. If the monitoring results indicate the TEQ level(s) merits limitation pursuant to 40 CFR 122.44(d) then the permit may be reopened (according to 40 CFR Part 122.62(a)) and the effluent limit(s) adjusted appropriately. Overall, the TEQ approach offers an additional tool for monitoring, assessing, and limiting the relative toxic effects and risks of all isomers of dioxins and furans, including 2,3,7,8-TCDD and TCDF.

Analytical Methods and Detection Levels

The March 15, 1989 guidance recommended that where calculated water quality-based limitations are less than the detection level for the analytical method, the calculated limit should be included in the permit. The memorandum also stated that the detection level of the analytical method should be the threshold for compliance/noncompliance determinations. While the overall thrust of those recommendations is still accurate, additional information has become available since that memorandum and is discussed below.

Analytical Methods

EPA regulations found at 40 CFR 122.41(j)(4) require that "monitoring results must be conducted according to test procedures approved under 40 CFR Part 136... unless other test procedures have been specified in the permit." The analytical method currently specified in 40 CFR Part 136 for dioxin is EPA method 613. Method 613 is a low resolution method incapable of detecting dioxin in the range of many of the recently developed water quality-based limitations. Therefore, it would be inappropriate to include method 613 in current pulp and paper mill permits. Instead, EPA recommends U.S. EPA method 1613 as the analytical method which should be specified in permits in conjunction with numerical permit limitations for 2,3,7,8-TCDD and limitations and/or monitoring requirements for other PHDDs and PHDFs. Thus, method 1613 should be specified on a permit-specific basis citing the authority of 40 CFR 122.41(j)(4) and 122.44(i)(1)(iv). This high resolution method was not available at the time of the March 15, 1989 guidance. Although this method has not yet been formally promulgated and published in 40 CFR Part 136, its use is recommended. EPA method 1613 can also be used to determine other dioxin/furan congeners in effluents.

The National Council for Air and Stream Improvement (NCASI) (a research arm of the pulp and paper industry) developed NCASI method 551 as a high resolution method which was utilized for analyses of 2,3,7,8-TCDD and 2,3,7,8-TCDF in the 104 Mill Study. The latest edition of EPA method 1613 and the method described in NCASI Technical Bulletin 551 produce comparable results for 2,3,7,8-TCDD and 2,3,7,8-TCDF when performed by qualified laboratories. Permitting authorities should specify method 1613 or, where requested, allow a permittee to employ NCASI method 551 as an equivalent method for 2,3,7,8-TCDD and 2,3,7,8-TCDF only. The Agency is not recommending at this time the use of method 551 as an equivalent method for the other dioxin and furan congeners because the necessary performance data and written protocol for the other congeners, although requested, has not been received.

Both EPA method 1613 and NCASI method 551 rely on high resolution gas chromatograph/mass spectrometer techniques which are relatively more expensive than many other types of analyses. Cost of analyses should be one of the factors considered by regulatory authorities when determining monitoring frequencies for a permit limitation or when requiring monitoring only.

Detection Levels

The March 15, 1989 guidance referred to the "detection level" as the level for compliance/noncompliance determinations. Based upon discussions with Regions and States, today's strategy recommends that permit writers specify the "minimum level" (ML) in permits that limit 2,3,7,8-TCDD as the "detection level" (i.e., the level at which compliance/noncompliance determinations will be made). EPA prefers this approach because the ML is conservative with respect to the determination of compliance with limits which are below the detection level. EPA's Industrial Technology Division has applied the ML in determinations of pollutant measurements by gas chromatography combined with mass spectrometry (GC/MS). The concept of a minimum level has been utilized in developing effluent limitations guidelines, most recently in the Organic Chemicals Plastics and Synthetic Fibers (OCPSF) effluent guidelines rulemaking (52 FR 42562).

The ML is defined as the "level at which the entire analytical system shall give recognizable mass spectra and acceptable calibration points." This level corresponds to the lowest point at which the calibration curve is determined. The calibration curve is determined on the basis of analyses for the pollutant of concern in a reagent water. The ML for 2,3,7,8-TCDD in reagent water using method 1613 is 10 ppq.

A review of data from the 104 Mill Study conducted by the pulp and paper industry demonstrates that measurement at the 10 ppq level is achievable by qualified laboratories. The value of 10 ppq was established in that study as the target detection level for 2,3,7,8-TCDD and 2,3,7,8-TCDF. A total of 31 measurements of 2,3,7,8-TCDD in pulp and paper industry effluents were reported as non-detects, with 80% of the detection levels associated with these non-detects less than or equal to 10 ppq. A total of 11 measurements of 2,3,7,8-TCDF in effluent were reported as non-detects with all detection levels at or below 10 ppq. Attachment 1 includes graphs of cumulative distributions of detection levels for the 104 Mill Study non-detect measurements for effluent 2,3,7,8-TCDD and 2,3,7,8-TCDF measurements. These cumulative distribution graphs show how the detection levels are distributed throughout the range of reported values.

EPA believes that the Minimum Level (ML) is a valid scientific and regulatory concept. The ML is the smallest concentration used in calibration of the measurement system. The

relationship established in the calibration process defines the manner in which measurements are quantified. Quantifying measurements below the ML requires extrapolation of the calibration relationship below the range of data used to establish the calibration. The Agency will continue to use the Minimum Level concept in establishing numerical limitations for the discharge of pollutants in wastewater.

The minimum level is not equivalent to the "method detection limit" (MDL) which is defined in 40 CFR Part 136 Appendix B as "the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte." The Agency's methodology for determining the MDL is described in 40 CFR Part 136, Appendix B. For 2,3,7,8-TCDD, the MDL of 5.6 ppq was determined using Agency methodology on the basis of a single laboratory study conducted by ITD. The permitting authority may choose to specify the MDL (which usually is more restrictive than the ML) as the level at which compliance/noncompliance determinations are made. Where the permitting authority elects to specify the MDL within a permit, the regulatory authority may employ the Agency determined value (5.6 ppq) or require a new MDL study.

Another approach sometimes considered in the development of regulatory requirements is referred to as the "Practical Quantitation Limit" (PQL). The PQL typically is set as a specific multiple of the MDL. EPA does not recommend the use of the PQL as the value for making compliance/noncompliance determinations in chlorine bleaching pulp and paper mill permits for PHDDs and PHDFs; instead, EPA recommends use of the ML for the reasons discussed above.

A recent discussion of the concepts related to detection limit/quantitation limit is contained in the 17th Edition of Standard Methods for the Examination of Water and Wastewater, 1989, Section 1030E, pages 1-18 to 1-20. This discussion includes the following statement on page 1-18: "Detection limits are controversial principally because of inadequate definition and confusion of terms." EPA believes that the use of the ML can avoid much of the confusion associated with terms such as Limit of Detection (LOD), Limit of Quantitation (LOQ), Practical Quantitation Limit (PQL) and Detection Limit. The ML and LOQ are approximately equal numerically with the degree of agreement depending on specific circumstances. The ML and LOQ are equivalent conceptually in the sense that values above the ML are considered to be quantified measurements.

Monitoring strategies associated with permit limitations which are below the minimum level

There are a number of additional approaches which should be considered and employed if appropriate where a calculated water quality-based limit is below the compliance level specified in the permit in order to help determine whether water quality standards are being attained or maintained. These approaches can be applied separately or in combination. Regulatory authorities should carefully consider the utility of each approach for specific situations and include such measures in permits where they believe these techniques will provide valuable information.

Use of internal waste stream limitations and monitoring points

Where final, end-of-pipe effluent limitations are determined to be impractical or infeasible to measure, permitting authorities can, in accordance with the requirements of 40 CFR 122.45(h), establish limitations for internal plant waste streams from bleached plant processes. Section 122.45(h) states that where the permit contains internal limits, the permit shall also require monitoring at the point where the limit applies. The rationale for internal waste stream limits is that levels of 2,3,7,8-TCDD (as well as other chlorinated organics) at a plant are highest in process waste streams where they are produced, before being diluted with other waste water flows. In addition, sufficiently accurate measurement of pollutant concentrations in the final effluent is not possible where the effluent limit is below the minimum level. It should be noted, however, that monitoring of internal waste streams may require establishment of a higher level at which compliance/noncompliance determinations will be made (due to matrix effects) than is used for final effluents. Limitations on internal waste streams should only be imposed where they can be related to the calculated end-of-pipe loading, accounting for demonstrated removals of 2,3,7,8-TCDD by the wastewater treatment facility. The fact sheet for the permit should set forth the specific circumstances which make limitations on internal waste streams necessary in accordance with the requirements of 122.45(h). The permitting authority may choose to require internal waste stream monitoring without internal waste stream limits to provide an indication of PHDD/PHDF levels at the end of the bleach process.

Furan (2,3,7,8-TCDF) as an indicator of dioxin (2,3,7,8-TCDD) levels

2,3,7,8-TCDF concentrations tend to be at least an order of magnitude higher than 2,3,7,8-TCDD concentrations for many chlorine bleaching pulp and paper mill effluents. This relationship is different for different mills, but can be expected to be relatively constant for a particular mill as long as a mill's production processes remain the same. Thus, where

the relationship can be quantified, 2,3,7,8-TCDF concentrations might serve as an indicator of 2,3,7,8-TCDD levels or could be used to establish wastewater treatment plant removal efficiencies in cases where permitted 2,3,7,8-TCDD levels are below detection levels. 2,3,7,8-TCDF should be monitored in effluents and may also be monitored in fish tissues, sludge, and pulp to gather additional information. EPA method 1613 should be used as the analytical method for such monitoring.

Fish or shellfish tissue analysis

Dioxins and furans are highly bioaccumulative. Because of this, aquatic organisms can serve as valuable indicators of whether effluent levels below detection are of concern and are causing excursions above narrative or numeric water quality standards. For this reason, fish or shellfish tissue analyses are strongly encouraged in most discharge situations.

Several general approaches are possible. These include exposing aquatic organisms to various effluent concentrations or sediment in the laboratory in accordance with standard test protocols; ambient studies where resident fish in the receiving waters would be collected and analyzed; and ambient studies which utilize caged organisms placed at desired locations within the receiving stream. There are advantages and disadvantages associated with the various types of fish or shellfish studies. Attachment 5 provides a more detailed discussion of the various options.

Regulatory authorities should exercise caution in interpreting and applying the results of fish tissue analysis. For example, contaminated sediments can sometimes contribute to fish tissue contamination and thus affect fish tissue analyses. Any constraints inherent in the study plan as well as quality assurance/quality control information should be considered in evaluating sample results. Regulatory authorities may use permittees' fish tissue data in a number of different ways where such data are deemed to be representative of the current discharge.

First, since fish bioaccumulate dioxins and furans, data may serve as a check on the effectiveness of effluent limits and appropriateness of monitoring frequencies. Fish tissue data can serve as a check for whether the water quality standard is being attained. For permits where the gap between the calculated permit limit (which protects against violations of water quality standards) and the detection level specified in the permit is large, tissue monitoring data can reveal whether or not controls implemented to achieve standards are sufficient. If data reveal that controls do not effectively achieve standards (tissues continue to show unacceptable contamination) even though dioxins or furans are not detected using appropriate methods, further

control actions may be warranted. Second, data indicating tissue levels of concern may be used as a tool to trigger re-examination of mill operating records or mill treatment system performance. Third, tissue data can be used as a trigger for issuance of local health advisories or to initiate clean-up actions. Finally, where numeric effluent limits are not yet in place, these data can be used for determining whether a water quality standard is likely to be exceeded, and thus, whether water quality-based limits are necessary.

FURTHER GUIDANCE AND ASSISTANCE

This strategy represents EPA's guidance for assessing and controlling discharges of PHDDs and PHDFs from chlorine bleaching pulp and paper mills and in some cases chlorinated organics. Numerous ongoing studies and evaluations are referenced in this strategy. As these and other data become available, EPA will forward this information to regulatory authorities along with any specific guidance relative to its use. EPA will also work with regulatory authorities to provide assistance in implementing this strategy.

Attachments

1) USEPA Method 1613 Summary
2) Sample Special Permit Conditions for Chlorinated Organics Reduction and Monitoring Program for Chemical Pulp Mills that Bleach with Chlorine
3) AOX Used as a Surrogate Measure of Chlorinated Organics
4) Toxicity Equivalent Factors for Dioxin and Furan Congeners
5) Fish Tissue Analysis for Dioxins/Furans

Attachment 1

USEPA METHOD 1613 SUMMARY

Introduction

Method 1613 is a high resolution capillary column gas chromatography (HRGC)/high resolution mass spectrometry (HRMS) method for analysis of tetra- through octa- chlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) using isotope dilution. Method 1613 was developed by the Industrial Technology Division (ITD) within the United States Environmental Protection Agency's (USEPA) Office of Water Regulations and Standards (OWRS) to provide improved precision and accuracy of analysis of pollutants in aqueous and solid matrices. The ITD is responsible for development and promulgation of nationwide effluent limitation guidelines for pollutant levels in industrial discharges.

Scope and Application

Method 1613 is designed to meet the survey requirements of the USEPA ITD. The Method is used to determine the tetra- through octa- chlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) associated with the Clean Water Act (as amended 1987); the Resource Conservation and Recovery Act (as amended 1986); and the Comprehensive Environmental Response, Compensation and Liability Act (as amended 1986); and other dioxin and furan compounds amenable to high resolution capillary column gas chromatography (HRGC)/high resolution mass spectrometry (HRMS). Specificity is provided for determination of the 2,3,7,8- substituted isomers of polychlorodibenzo-p-dioxin (PCDD) and polychlorodibenzofuran (PCDF). The Method is based on EPA, industry, commercial laboratory, and academic methods (References 1 - 6).

The compounds listed in Table 1 may be determined in waters, soils, sludges, and other matrices by Method 1613. The detection limits of the Method are usually dependent on the level of interferences rather than instrumental limitations. The levels in Table 1 typify the minimum quantities that can be detected with no interferences present.

The GCMS portions of the Method are for use only by analysts experienced with HRGC/HRMS or under the close supervision of such qualified persons. Each laboratory that uses Method 1613 must demonstrate the ability to generate acceptable results using the procedure in Section 8.2 of the Method.

Summary of Method

Stable isotopically labeled analogs of fifteen of the PCDDs and PCDFs are added to each sample. Samples containing coarse solids are prepared for extraction by grinding or homogenization. Water samples are filtered and then extracted with methylene chloride using separatory funnel procedures; the particulates from the water samples, soils, and other finely divided solids are extracted using a combined Soxhlet extraction/Dean-Stark azeotropic distillation (Reference 7). Prior to cleanup and analysis, the extracts of the filtered water and the particulates are combined.

After extraction, $^{37}Cl_4$-labeled 2,3,7,8-TCDD is added to each extract to measure the efficiency of the cleanup process. Sample cleanup may include back extraction with acid and/or base, and gel permeation, alumina, silica gel, and activated carbon chromatography. High performance liquid chromatography (HPLC) can be used for further isolation of the 2,3,7,8- isomers or other specific isomers or congeners.

After cleanup, the extract is concentrated to near dryness. Immediately prior to injection, two internal standards are added to each extract, and a 1 uL aliquot of the extract is injected into the gas chromatograph. The analytes are separated by the GC and detected by a high resolution ($\geq$10,000) mass spectrometer. The labeled compounds serve to correct for the variability of the analytical technique.

Dioxins and furans are identified by comparing GC retention times and the ion abundance ratios of the m/z's with the corresponding retention time ranges of authentic standards and the theoretical ion abundance ratios of the exact m/z's. Isomers and congeners are identified when the retention times and m/z abundance ratios agree within pre-defined limits. By using a GC column or columns capable of resolving the 2,3,7,8-substituted isomers from all other isomers, the 2,3,7,8-substituted isomers are identified when the retention time and m/z abundance ratios agree within pre-defined limits of the retention times and exact m/z ratios of authentic standards.

Quantitative analysis is performed by GCMS using selected ion current profile (SICP) areas, in one of two ways: 1) For the fifteen 2,3,7,8-substituted isomers for which labeled analogs are available (see Table 1), the GCMS system is calibrated and the compound concentration is determined using an isotope dilution technique; 2) For non-2,3,7,8-substituted isomers and the total concentrations of all isomers within a level of chlorination (i.e., total TCDD), concentrations are determined assuming response factors from the calibration of labeled analogs at the same level of chlorination. Although a labeled analog of the octachlorinated dibenzofuran (OCDF) is available, using high resolution mass spectrometry, it produces an m/z that may interfere with the identification and quantitation of the native

octachlorinated dibenzo-p-dioxin (OCDD). Therefore, this labeled analog has not been included in the calibration standards, and the native OCDF is quantitated against the labeled OCDD. The labeled analog of 1,2,3,6,7,8-HxCDD is added to the extracts immediately prior to analysis, and is used as an internal standard. As a result, this analog cannot be used to quantify the native 1,2,3,6,7,8-HxCDD by isotope dilution. Therefore, this native isomer is quantitated against the other two labeled HxCDD analogs.

The quality of the analysis is assured through reproducible calibration and testing of the extraction, cleanup, and GCMS systems.

Quality Control

Each laboratory that uses Method 1613 is required to operate a formal quality assurance program (Reference 16). The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with labeled compounds to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the Method. If the Method is to be applied routinely to samples containing high solids with very little moisture (e.g., soils, filter cake, compost) or to an alternate matrix, the high solids reference matrix or the alternate matrix is substituted for the reagent water matrix in all performance tests.

Method Development, Validation and Promulgation

Method 1613 was originally developed by ITD in the summer of 1988 to increase the quality of data collected and provide a QA/QC program consistent with other ITD survey methods. ITD survey methods contain QA/QC programs that equal or exceed the 600 Series [304(h)] standard. The current revision is a result of extensive peer review and comment, intralaboratory validation, and analysis of over 500 samples of industrial and municipal waste waters and sludges.

ITD has conducted a single laboratory validation of the Method and the SDS extraction technique for municipal sewage sludge. A single laboratory validation of the Method for paper pulp is currently in progress.

A multiple laboratory validation study is scheduled to start in May 1990. More than fourteen laboratories from four countries are scheduled to participate in this study.

As part of the Method's ongoing QA/QC requirements and ITD's QA/QC program, ITD and each laboratory performing Method 1613 routinely collect data on method performance in various reference

matrices (see Section 6.6 of the Method). Additional method performance data were collected by ITD during 1989 industry studies on effluent and sludge samples from the pulp and paper, petroleum refining, superfund dischargers, and pesticides industries.

Currently, Method performance data are being compiled into a summary report for submission to EMSL Cincinnati for interim approval under Section 304(h) of the Clean Water Act.

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16 "Handbook of Analytical Quality Control in Water and Waste water Laboratories," USEPA, EMSL, Cincinnati, OH 45268, EPA-600/4-79-019 (March 1979).

17 "Standard Practice for Sampling Water," ASTM Annual Book of Standards, ASTM, Philadelphia, PA, 76 (1980).

18 "Methods 330.4 and 330.5 for Total Residual Chlorine," USEPA, EMSL, Cincinnati, OH 45268, EPA 600/4-70-020 (March 1979).

Table 1
PCDD AND PCDF COMPOUNDS DETERMINED BY METHOD 1613

Native Compound(1)	Labeled Analog	Minimum Level(2) Water pg/L ppq	Solid ng/kg ppt	Extract pg/uL ppb
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF	10	1	0.5
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD	10	1	0.5
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF	50	5	2.5
2,3,4,7,8-PeCDF	$^{13}C_{12}$-2,3,4,7,8-PeCDF	50	5	2.5
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD	50	5	2.5
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	50	5	2.5
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	50	5	2.5
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	50	5	2.5
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	50	5	2.5
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	50	5	2.5
1,2,3,7,8,9-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD(3)	50	5	2.5
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	50	5	2.5
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	50	5	2.5
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	50	5	2.5
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	50	5	2.5
OCDD	$^{13}C_{12}$-OCDD	100	10	5.0
OCDF	$^{13}C_{12}$-OCDD	100	10	5.0

(1) Polychlorinated dioxins and furans:

TCDD = Tetrachlorodibenzo-p-dioxin
TCDF = Tetrachlorodibenzofuran
PeCDD = Pentachlorodibenzo-p-dioxin
PeCDF = Pentachlorodibenzofuran
HxCDD = Hexachlorodibenzo-p-dioxin
HxCDF = Hexachlorodibenzofuran
HpCDD = Heptachlorodibenzo-p-dioxin
HpCDF = Heptachlorodibenzofuran
OCDD = Octachlorodibenzo-p-dioxin
OCDF = Octachlorodibenzofuran

(2) Level at which the analytical system will give acceptable SICP and calibration.

(3) Labeled analog is used as an internal standard and therefore cannot be used for quantitation by isotope dilution.

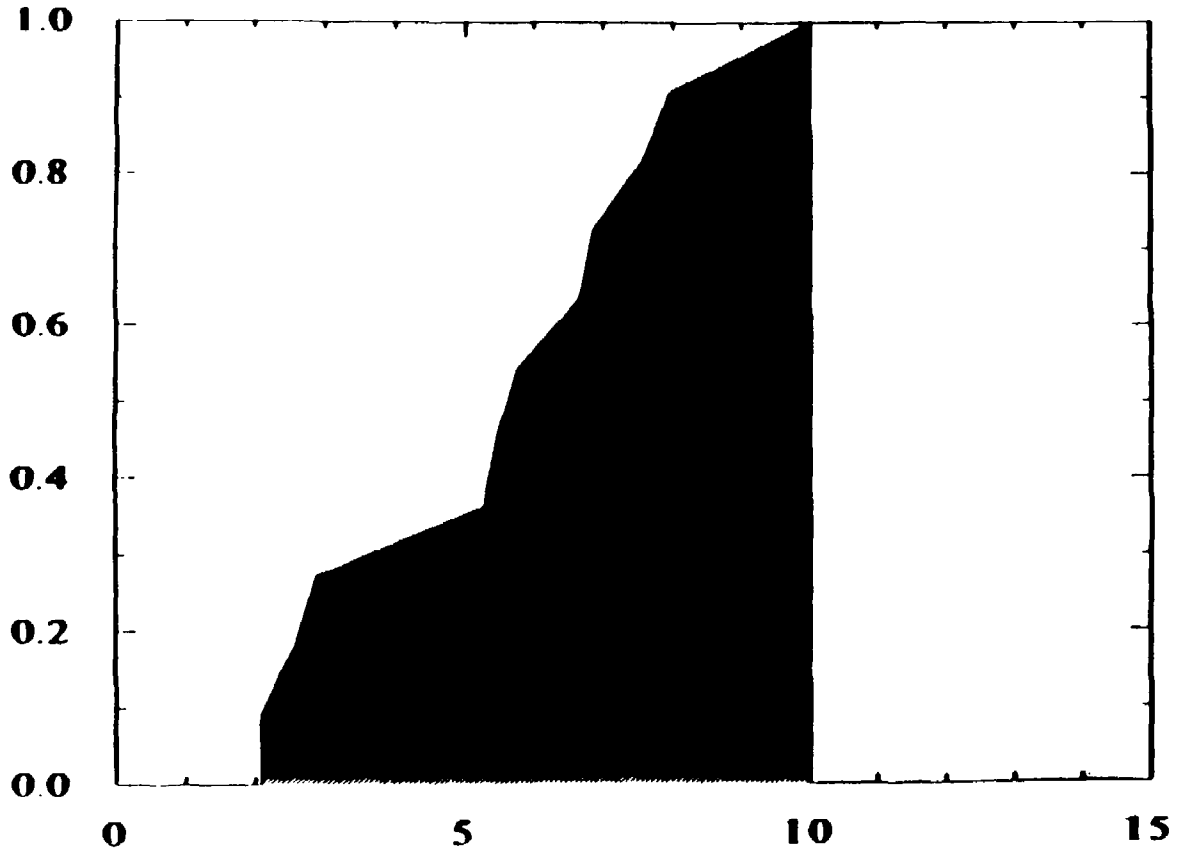
Cum. Proportion of Detection Level

104 MILL STUDY

USEPA/PAPER INDUSTRY COOPERATIVE DIOXIN STUDY

SAMPLE CUMULATIVE DISTRIBUTION GRAPH

EFFLUENT TCDF DETECTION LEVEL VALUES



Conc of 2378-TCDF (in PPQ)

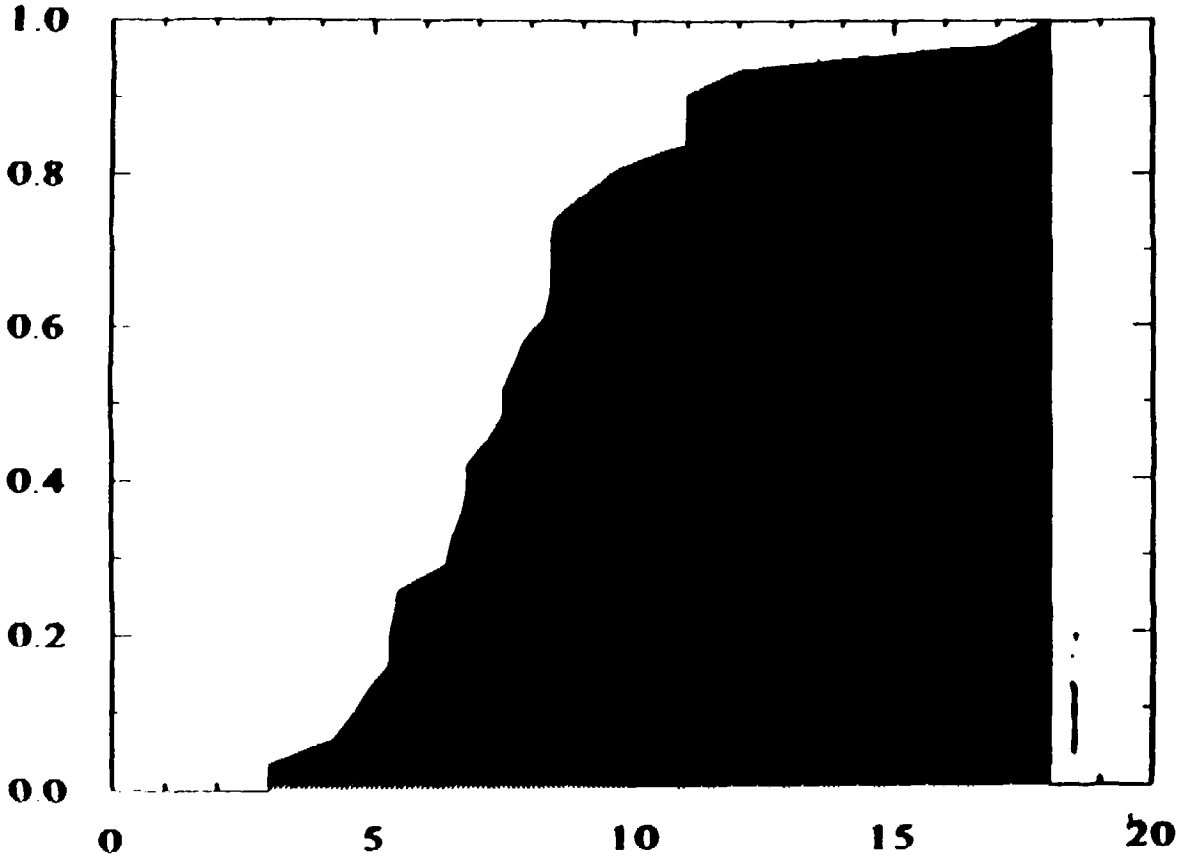
Cum. Proportion of Detection Level

104 [illegible]L STUDY

USEPA/PAPER INDUSTRY COOPERATIVE DIOXIN STUDY

SAMPLE CUMULATIVE DISTRIBUTION GRAPH

EFFLUENT TCDD DETECTION LEVEL VALUES



Conc. of 2378-TCDD (in PPQ)

Attachment 2

EXAMPLE

CHLORINATED ORGANICS REDUCTION AND MONITORING PROGRAM FOR CHEMICAL PULP MILLS THAT BLEACH WITH CHLORINE

A. CHLORINATED ORGANICS REDUCTION PROGRAM

Beginning not later than 60 days from the effective date of this permit, the Permittee shall submit to the permitting agency a Chlorinated Organics Reduction Program showing how the permittee, in the short term intends to meet the chlorinated organics limitations contained in this permit. The objectives of the program should be (1) to reduce, to at least the extent required to meet all permit limitations, formation of 2,3,7,8-TCDD, 2,3,7,8-TCDF in pulping and bleaching operations through process changes and process modifications; and (2) to reduce the discharge of 2,3,7,8-TCDD, 2,3,7,8-TCDF through changes in waste water treatment system operations. The scope of the Chlorinated Organics Reduction Program is intended to encompass changes that can be made in relatively short periods of time at relatively low levels of capital funding. However, the Permittee should include in its submitted program longer term capital intensive projects that are planned or under construction.

As a minimum, the Program shall address whether each of the following items is appropriate and feasible:

PULPING

1. Discontinuing the use of pitch dispersants and brown stock defoamers which may contain chlorinated dioxin and chlorinated furan precursor compounds.

2. Maximizing delignification in the pulping process within the capability of available equipment.

3. Maximizing brownstock pulp washing efficiency to achieve the lowest possible washing loss (measured as pounds Na_2SO_4 per ton of pulp)

4. Elimination of the use of foul condensates for brownstock pulp washing.

BLEACHING

1. Reducing the chlorine multiple (Kappa factor), with a target value of less than 0.15.

2. Maximizing chlorine dioxide substitution for chlorine in the first stage of bleaching.

3. Eliminating or minimizing the use of hypochlorite through substitution with hydrogen peroxide and other chemicals.

4. Providing for hydrogen peroxide reinforced oxygen extraction in all extraction stages and prior to chlorination.

5. Installing chlorination residual sensors and controllers to improve chlorination control and eliminate localized overchlorination.

6. Installing on-line Kappa monitoring to assist in controlling the chlorine multiple.

7. Providing for split addition of chlorine/chloride dioxide with PH adjustment.

OTHER IN-PLANT

1. Alter cleaning procedures such that no chlorine-based bleaches are used for cleaning of process equipment.

2. Substituting chlorine dioxide for chlorine for use as a slimicide/fungicide.

3. Investigating and implementing of process waste water flow reduction and water conservation practices for all mill operations (e.g., wood yard, pulping and chemical recovery, bleaching, papermaking).

WASTE WATER TREATMENT

1. Investigating utilization of polymers and/or coagulants to provide improved TSS removal,or otherwise provide for improved TSS removal in waste water treatment facilities. Within 180 days from the effective date of this permit and continuing every three months thereafter through the life of the permit, the Permittee shall submit a report describing the status of the above program. Such report shall describe which actions have been taken to date and which actions will be undertaken along with a projected completion date and the anticipated results expected from completion of the action. The report shall be specific as to changes in pulping operations; bleaching operations (bleaching sequence, chemical application rates, chlorine ratio, percent chlorine dioxide substitution, etc.); waste water flow reduction; waste water treatment operations, etc. All items on the above list shall be addressed. In the event that the Permittee has not or does not intend to implement the above referenced actions, a detailed explanation including supporting data shall be provided showing the basis of such decision for each action not implemented.

B. QUARTERLY TESTING PROGRAM AND PROGRESS REPORTING

1. Once per quarter, the Permittee shall conduct a 72-hour sampling program at each bleach line, the final effluent and waste water sludge from the permitted facility. The purpose of the monitoring program is to document current rates of formation of 2378-TCDD, 2378-TCDF and AOX, and characterize the final effluent and sludge in terms of TSS, AOX, 2378-TCDD and 2378-TCDF.

2. Seventy-two hour composite samples shall be obtained at the following locations:

Each Bleach Line

- Fully Bleached Pulp
- Combined Bleach Plant waste waters prior to mixing with other process waste waters and on-contact cooling waters. Individual bleach plant filtrates may be sampled and composited on a flow-weighted basis prior to analysis, or analyzed separately. (Installation of flow monitoring equipment for bleach plant process waste waters may be necessary).

Waste water Treatment Sludges

- Combined primary and secondary dewatered sludge or other sludge removed from the waste water treatment system.

3. Three consecutive 24-hour composite samples shall be obtained at the following location and shall be analyzed individually:

Final Effluent

- Final treated process waste water effluent prior to discharge and prior to mixing with non-contact cooling waters.

4. The Permittee shall determine mass flow rates of sampled waste waters and pulps and shall record process information during the sampling event as required for the USEPA/Paper Industry Cooperative Dioxin Study (104 Mill Study). For swing lines, separate bleached pulp and bleach plant waste water samples shall be obtained for each type of pulp bleached.

5. Samples shall be analyzed for 2378-TCDD and 2378-TCDF by USEPA Method 1613 or other methods explicitly approved by USEPA. Samples shall be analyzed for AOX by method ISO/DIS 9562 or Scan W-9:89 until an U.S. EPA AOX method is formally promulgated.

6. The Permittee shall report the results of the monitoring program and the process information for each 72 hour sampling event not later than 60 days after the end of each calendar quarter.

Attachment 3

AOX Used as a Surrogate Measure of Chlorinated Organics

Recently, there has been increasing concern about the environmental impact of chlorinated organics, such as dioxin and furan, created in the pulping and bleaching processes. These compounds are not completely decomposed or destroyed in the conventional biological treatment processes and are subsequently released into the receiving water bodies. Some of these compounds, such as resin acids and chlorinated guaiacol, are toxic to fish and other aquatic organisms, while some of the others contribute to carcinogenicity and mutagenicity. Furthermore, some recent scientific research and studies indicate that some of the chlorinated organics with high molecular weights and which were thought to be biologically inactive, have been found to be broken down by certain bacteria into low molecular weight chlorinated organics possibly having detrimental biological effects.

An analytical parameter now being evaluated as a monitoring tool and as a measure of the chlorinated organics in the discharge(s) is Adsorbable Organic Halogens (AOX). AOX and dioxin are both related to the amount of chlorine used in the bleaching process; however, to date a relationship between AOX and dioxin has not been developed. Canadian, Scandinavian and EPA experts believe that achievement of 1.5 kg of AOX per metric ton of pulp production could result in substantial reductions in the levels of dioxin and furans in effluent, pulp, and sludges.

One of the presently preferred methodology in this country for the reduction of dioxins is to reduce the amount of chlorine used through substitution of chlorine dioxide for chlorine. However, low levels of substitution (10-50 percent) may result in variable decreases in the amount of chlorinated organics total produced, and can actually result in an increase in the levels of chlorinated phenolics. However, where greater than 50 percent substitution is practiced, substantial reductions in chlorinated organics are achieved. Process changes such as oxygen delignification, extended delignification, improved brownstock washing, oxygen extraction and peroxide reinforced extraction result in reductions in chlorinated organics as well as dioxin.

Regulations for the control of chlorinated organics measured as AOX have been established or are in preparation in Norway, Finland, West Germany and Canada. Regulations in Sweden are based on TOCl, which is a measurement of the total organically-bound chloride in the process effluent. However, compliance will be performed using AOX and an AOX/TOCl correlation to be established for each facility. The Swedish government has set a goal for their paper industries requiring that mills reduce their

generation of chlorinated compounds via a phased reduction program and ultimately attain a maximum discharge of 0.1 kg TOCl/metric ton of bleached pulp by the year 2010. (For comparative purposes, AOX is approximately 1.4 times TOCL.) The Canadian provinces of British Columbia, Ontario and Quebec have established interim AOX limitations of 2.5 kg/metric ton and a final limitation of 1.5 kg/metric ton. The Province of Alberta has indicated that it intends to establish its regulation at 1.0 kg/metric ton and the federal government of Canada is preparing regulations which will limit AOX at 1.5 kg/metric ton.

In the United States, wastewater control criteria have not yet been developed and EPA is considering including AOX in the revised technology-based regulations that are under development. Following the leads of the Canadian Federal and Provincial governments, the States of Oregon and Washington are developing BPJ/BAT effluent limitations for AOX of 1.5 kg/metric ton of production. Initial research and monitoring studies done by the State of Oregon suggest that the existing mills in Oregon could achieve 1.5 kg of AOX/metric ton after they have been upgraded with the best available technology for controlling chlorinated organics. Further background information is available in a document entitled, "Best Professional Judgement on the Control of Chlorinated Compounds from the Pulp and Paper Industries (1/24/90)" prepared by the Oregon Department of Environmental Quality.

EPA's approach to the regulation of AOX is to develop a method specific to the determination of AOX in wastewater, adapted from existing methods. EPA plans to incorporate standardized quality assurance/quality control into the AOX method. This standardized QA/QC is not present in existing AOX methods, such as Scandinavian Pulp and Paper Board method Scan W-9:89 and ISO/DIS method 9562. A draft EPA AOX method in EMSL-Cincinnati format and containing a 600 series QC program is scheduled for release in July 1990. This method is being developed based on the currently available methods referenced above and data collected to date from analysis of pulp and paper industry wastewaters. The EPA AOX method is scheduled for proposal under Section 304(h) of the CWA in the fall of 1990. Preliminary development has revealed that an AOX method using a batch adsorption procedure is preferable to the Total Organic Halogen (TOX) method because the AOX method provides more reproducible results for pulp and paper industry samples in which finely divided particles are present. Further, the TOX procedure employs carbon columns that are subject to plugging by the particulates and are susceptible to channeling, resulting in more variable results.

Until U.S. EPA promulgates its approved AOX analytical method it is recommended that the "International Standards Organization" (ISO/DIS 9562) method or the Scan W-9:89 method be

cited in permits. A copy of the ISO and Scan AOX analytical methods may be obtained by contacting the Office of Water's Industrial Technology Division at (202) 382-7120.

Attachment 4

Table 2. Toxicity Equivalency Factors

Compound	EPA-TEFs/87	I-TEFs/88
Mono-, Di-, and TriCDDs	0	0
2,3,7,8-TCDD	1	1
Other TCDDs	0.01	0
2,3,7,8-PeCDD	0.5	0.5
Other PeCDDs	0.005	0
2378-HxCDDs	0.04	0.1
Other HxCDDs	0.0004	0
2,3,7,8-HpCDD	0.001	0.01
Other HpCDDs	0.00001	0
OCDD	0	0.001
Mono-, Di-, and TriCDFs	0	0
2,3,7,8-TCDF	0.1	0.1
Other TCDFs	0.001	0
1,2,3,7,8-PeCDF	0.1	0.05
2,3,4,7,8-PeCDF	0.1	0.5
Other PeCDFs	0.001	0
2378-HxCDFs	0.01	0.1
Other HxCDFs	0.0001	0
2378-HpCDFs	0.001	0.01
Other HpCDFs	0.00001	0
OCDF	0	0.001

Reference: Adapted from NATO/CCMS, 1988a.

(U.S. EPA's "Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-Dioxins and -Dibenzofurans (CDDs and CDFs) and 1989 Update, EPA/625/3-89/016, March 1989)

Attachment 5

Fish Tissue Analysis for Dioxins/Furans

Regulatory authorities can consider requiring permittees to sample fish tissues for contamination from pulp mills where effluent levels of dioxins/furans may be below limits of detection. Fish tissue data can provide an indirect compliance tool which can supplement existing effluent limitations by helping to ensure adequate monitoring and detection. Possible types of tissue studies as well as potential uses of fish tissue data in a regulatory context are discussed below.

Study Types

A number of different types of fish tissue studies have been proposed. These include resident fish sampling, caged fish ambient exposures, and laboratory exposures to effluent or sediment. All of the study types and their drawbacks are discussed below.

1) Resident Fish

For resident fish sampling studies, a number of geographic, species-related, and data quality considerations apply. Sampling sites should be located near mill outfalls to ensure that fish sampled have been maximally exposed to mill effluents. To enhance the probability of detecting dioxin in the aquatic environment, analyses are recommended for fish representing the largest and oldest specimens to provide the best indicator of the potential impacts on aquatic life and human health. Nonmigratory species are preferred, but if migratory fish are used, fish should not be collected during the migratory season. Similarly, spawning season should be avoided.

Criteria to be considered for selection of fish species to be sampled should include habitat preference (e.g., areas of sediment deposition) and known accumulators (e.g. carp, catfish, walleye, bass). If composite samples are used, individual specimens should be of similar size. As an indicator of the presence of dioxin, whole body analysis is preferred over filet analysis. Analysis of some target organs (e.g., liver) could serve as a more sensitive indicator than whole body. Fish from a "clean" control site should also be analyzed for comparison. For further information on sample study design, see EPA's "Assessing Human Health Risks from Chemically Contaminated Fish and Shellfish; A Guidance Manual" (EPA-503/8-89-002).

For performing resident fish sampling, EPA recommends the following quality assurance/quality control requirements:

1. Standardized written sampling and analytical procedures.

2. Standardized handling and shipping procedures.

3. Use of blanks (reagent and field).

4. Use of spiked samples to control accuracy and internal standards to quantify target analytes.

5. Specified calibration procedures to control accuracy and verify detection limits.

6. Standardized data reduction and validation procedures.

2) Caged Fish

A proposed alternative to resident fish sampling is to conduct sampling via "caged fish" exposures to effluents. However, applying this type of study to mill effluents where dioxin is expected to be present may be problematic. First, caged fish are excluded from natural contact sediment, a potentially significant route of exposure. Second, it may be difficult to successfully keep caged fish alive for several months to meet the long exposure time necessary for dioxin to bioaccumulate to detectable levels in tissue.

3) Laboratory Studies

The third possible study type is to expose fish to mill effluent in a laboratory setting (see American Society of Testing and Materials, "Standard Practice for Conducting Bioconcentration Tests with Fishes and Saltwater Bivalve Mollusks", Designation E1022-84, 1986, Annual Book of ASTM Standards, vol. 11.04, 01-110485-48, pp. 702-724, 1985). There are a number of potential problems associated with this approach: difficulty of maintaining healthy organisms during moderately high dioxin effluent exposure due to dioxin's extreme toxicity; adapting the test to a complex effluent mixture when it was originally designed to test a single compound at a time; and accounting for differences in bioconcentration factors and exposure durations necessary for dioxin to reach equilibrium among different species.

Another proposed laboratory method for fish sampling is exposure of fish in the laboratory to ambient dioxin-contaminated sediment. This approach is also difficult to apply and interpret, since the link between tissue levels from exposure to sediment and tissue levels of resident fish from the same water body has not yet been established (see D.W. Kuehl, et al., "Bioavailability of Polychlorinated Dibenzo-p-dioxins and dibenzofurans from Contaminated Wisconsin River Sediment to

Carp", Chemosphere, Vol. 16, No. 4, pp. 667-679, 1987). Moreover, there are difficulties in characterizing sediment composition and in compositing a representative sample.