INVESTIGATION

- CONSISTED OF SEVEN TIERS

TIER 1 -- 2,4,5-TRICHLOROPHENOL (2,4,5-TCP) PRODUCTION SITES (AND ASSOCIATED WASTE DISPOSAL SITES)

2 -- SITES WHERE 2,4,5-TCP WAS USED AS A PRECURSOR TO MAKE PESTICIDAL PRODUCTS (AND ASSOCIATED WASTE DISPOSAL SITES)

3 -- SITES WHERE 2,4,5-TCP AND ITS DERIVATIVES WERE FORMULATED INTO PESTICIDAL PRODUCTS

4 -- COMBUSTION SOURCES

5 -- SITES WHERE PESTICIDES DERIVED FROM 2,4,5-TCP WERE USED

6 -- PRODUCTION SITES FOR OTHER CHEMICALS WHERE 2,3,7,8-TCDD FORMATION MAY HAVE OCCURRED

7 -- BACKGROUND (URBAN/RURAL SOIL, FISH SAMPLES)

RESULTS

TIERS 1 AND 2 - PRODUCTION AND DISPOSAL SITES

- 100 PRODUCTION/DISPOSAL SITES IDENTIFIED (Fewer than the 400-500 projected)
  - 21 2,4,5-TCP RELATED PRODUCTION FACILITIES
  - 79 ASSOCIATED WASTE DISPOSAL SITES (most are in Missouri)
- THESE SITES GENERALLY HAD THE HIGHEST LEVELS AND GREATEST QUANTITIES OF 2,3,7,8-TCDD
  - IN A NUMBER OF CASES, OFFSITE MIGRATION HAS OCCURRED
  - A NUMBER OF FISH ADVISORIES HAVE BEEN ISSUED AS A RESULT OF CONTAMINATION
  - FEDERAL, STATE AND RESPONSIBLE PARTIES HAVE INITIATED ACTION TO ADDRESS CONTAMINATED SITES AND CONTROL HUMAN EXPOSURE
  - LACK OF DISPOSAL CAPACITY HAMPERS IMPLEMENTATION OF PERMANENT REMEDIES

TIER 3 - PESTICIDE FORMULATORS

- GENERALLY NOT FOUND TO BE EXTENSIVELY CONTAMINATED ABOVE THE 1 PPB LEVEL (WITH THE EXCEPTION OF TWO LARGE FACILITIES) - I.E. 2,3,7,8-TCDD WAS USUALLY DETECTED IN ONLY ONE OR TWO SAMPLES AT A GIVEN SITE.

- EPA ESTIMATES THAT 10% OF THE 300-600 FORMULATORS OF PARTICULAR PESTICIDES MAY HAVE LEVELS GREATER THAN 1 PART PER BILLION (PPB)

- CONTAMINATED SITES HAVE BEEN REFERRED TO THE SUPERFUND PROGRAM FOR APPROPRIATE ACTION.

- REGIONAL OFFICES ARE ALSO FOLLOWING UP AT LARGE FORMULATORS NOT ORIGINALLY SELECTED FOR SAMPLING.

TIER 4 - COMBUSTION SOURCES

- TESTED FOR PRESENCE OF OTHER ISOMERS OF DIOXINS AND FURANS IN ADDITION TO 2,3,7,8-TCDD.

- 13 SOURCES TESTED (approximately $100k/test)
  - SIGNIFICANT VARIABILITY IN EMISSION LEVELS AND PROJECTED GROUND LEVEL CONCENTRATIONS
  - SECONDARY COPPER SMELTER WITH HIGHEST EMISSION LEVELS HAS BEEN PERMANENTLY CLOSED
  - EPA WORKING WITH STATE OF ILLINOIS TO FURTHER EVALUATE WIRE RECLAMATION INCINERATORS

- ASH SAMPLES WERE COLLECTED TO EVALUATE POSSIBLE USE AS A LESS EXPENSIVE SCREENING DEVICE - UNABLE TO ESTABLISH SPECIFIC CORRELATION

- SEPARATE REPORT TO CONGRESS ON MUNICIPAL WASTE COMBUSTOR (MWC) INCLUDING GUIDANCE ON OPTIMIZING COMBUSTION SO AS TO MINIMIZE DIOXIN EMISSIONS PUBLISHED JULY 1987.
  - EPA HAS PROPOSED TO REGULATE MWC EMISSIONS UNDER §111 - NEW SOURCE PERFORMANCE STANDARDS - OF THE CLEAN AIR ACT

TIER 5 - 2,4,5 TCP AND SILVEX USE SITES

- SAMPLES COLLECTED FROM RANGELANDS, RICE FIELDS, FORESTS, RIGHTS OF WAY
- PREDICTABLY, 2,3,7,8-TCDD FOUND MORE FREQUENTLY AT 'USE' SITES THAN AT 'BACKGROUND' SITES (TIER 7)
- SOIL AND SEDIMENT CONTAMINATION WAS DETECTED AT 15 OF THE 26 USE SITES SAMPLED, GENERALLY IN THE LOW PARTS PER TRILLION (PPT) RANGE
  - THE PRINCIPAL EXCEPTION WAS A SITE WHERE SAMPLES WERE TAKEN AT A HERBICIDE MIXING/LOADING AREA FOR HELICOPTER SPRAYING ACTIVITIES
- STATISTICAL EXTRAPOLATION NOT POSSIBLE DUE TO THE LARGE VARIETY OF USE SITUATIONS

TIER 6 - 'OTHER' CHEMICAL PLANTS

- NOT EXTENSIVELY CONTAMINATED WITH 2,3,7,8-TCDD
  - LEVELS GREATER THAN 1 PPB FOUND AT 3 OF 18 FACILITIES SAMPLED
    - -- 3 FACILITIES BELOW 1 PPB
    - -- 12 NON-DETECTABLE

TIER 7 - 'BACKGROUND' SITES

- 2,3,7,8-TCDD RARELY FOUND IN URBAN OR RURAL BACKGROUND SOILS AT THE PPT LEVEL
- 2,3,7,8-TCDD CONTAMINATION IN FISH ASSOCIATED WITH CHEMICAL INDUSTRY ACTIVITIES AND THE PULP AND PAPER INDUSTRY
  - 2,3,7,8-TCDD WAS DETECTED AT 112 OF THE 394 SITES
  - 2,3,7,8-TCDD WAS DETECTED IN 23 OF 29 GREAT LAKES FISH SAMPLES FISH ADVISORIES ARE ALREADY IN EFFECT FOR MANY AREAS DUE TO MIREX, PCB AND MERCURY CONTAMINATION.
- WHILE LEVELS AS HIGH AS 85 PPT IN WHOLE FISH AND 41 PPT IN FILETS WERE FOUND, ONLY FOUR SITES HAD LEVELS ABOVE 25 PPT (ONE FILET)
- A NUMBER OF FISH ADVISORIES WERE IN EFFECT PRIOR TO THE STUDY (E.G. THE PETENWELL FLOWAGE IN WISCONSIN AND THE TITTABAWASEE RIVER IN MICHIGAN. A NUMBER OF ADDITIONAL ADVISORIES HAVE BEEN ISSUED AS A RESULT OF THE STUDY (ANDROSCOGGIN R. IN MAINE, RAINY R. IN MINN. AND THE KANAWHA R. IN W.VA.)
  - STRINGENT DISCHARGE LIMITS HAVE BEEN ESTABLISHED FOR THE DOW CHEMICAL COMPANY PLANT IN MIDLAND, MICHIGAN
- FOLLOW-ON STUDIES HAVE BEEN INITIATED
  - EPA/AMERICAN PAPER INDUSTRY STUDY OF PULP AND PAPER INDUSTRY
  - BIOACCUMULATIVE POLLLUTANT STUDY

REGULATORY ACTIVITIES

- IMPOSED STRINGENT MANAGEMENT AND DISPOSAL REQUIREMENTS BY LISTING CERTAIN DIOXIN CONTAMINATED WASTES AS HAZARDOUS.

  - ADDITIONAL REGULATIONS PROVIDE FOR EVENTUAL BANNING OF SUCH WASTES FROM LAND DISPOSAL UNLESS THEY ARE FIRST TREATED.

- CANCELLED USE OF 2,4,5-T.

- PLACED ADDITIONAL RESTRICTIONS ON USE AND PLACEMENT OF PCB TRANSFORMERS. INTENDED TO PREVENT EXPOSURE TO DIOXINS/FURANS GENERATED DURING PCB FIRES.

- IMPOSED ADDITIONAL USE RESTRICTIONS AND PRODUCT CONTAMINANT LEVEL RESTRICTIONS ON WOOD PRESERVATIVE USES OF PENTACHLOROPHENOL (PCP), INORGANIC ARSENICAL COMPOUNDS AND CREOSOTE.

- INITIATED RULEMAKING UNDER THE TOXIC SUBSTANCES CONTROL ACT TO REQUIRE PRODUCERS TO PROVIDE INFORMATION ON POSSIBLE CONTAMINATION IN ADDITIONAL PRODUCTS AND WASTE STREAMS.

- EVALUATING ADDITIONAL WASTE STREAMS FROM PCP WOOD TREATMENT OPERATIONS FOR POSSIBLE HAZARDOUS WASTE DESIGNATION.

NATIONAL DIOXIN STUDY

- REQUESTED IN A $7.4M 1984 CONGRESSIONAL APPROPRIATION

- TWO-YEAR NATIONWIDE STUDY TO INVESTIGATE EXTENT OF DIOXIN (2,3,7,8-TCDD) CONTAMINATION

- STUDY CONDUCTED AS PART OF NATIONAL DIOXIN STRATEGY. STRATEGY WAS DEVELOPED TO COORDINATE INVESTIGATIVE, REMEDIAL AND REGULATORY ACTIVITIES

- THOUSANDS OF SAMPLES COLLECTED - DIFFICULT CHALLENGE TO PERFORM ROUTINE PART PER BILLION AND PART PER TRILLION ANALYSES IN A VARIETY OF ENVIRONMENTAL MATRICES

- CONFIRMED CONTAMINATION DATA HAS PREVIOUSLY BEEN COMMUNICATED TO APPROPRIATE STATE AND LOCAL OFFICIALS

- BACKDROP: HIGH LEVEL OF PUBLIC AND CONGRESSIONAL CONCERN

  INDUSTRIAL ACCIDENTS - SEVESO, ITALY
  NITRO, W.VA

  RESIDENTIAL EXPOSURE - TIMES BEACH, MO.
  LOVE CANAL, NY
  JACKSONVILLE, ARK.

  AGENT ORANGE LITIGATION BY VIETNAM VETERANS

SUMMARY

- EPA HAS AGGRESSIVELY IMPLEMENTED A STRATEGY TO ASSESS AND DEAL WITH THE PROBLEM OF 2,3,7,8-TCDD.

- FEWER SITES THAN ANTICIPATED WERE FOUND ASSOCIATED WITH PRODUCTION AND WASTE DISPOSAL OF 2,4,5-TCP.

- AS EXPECTED THE 2,4,5-TCP SITES GENERALLY POSE THE MOST SERIOUS PROBLEMS AND ARE BEING DEALT WITH UNDER EPA'S SUPERFUND PROGRAM.

- WE FOUND FISH CONTAMINATION IN ABOUT 25% OF THE SAMPLES, PRINCIPALLY ASSOCIATED WITH LARGER RIVER SYSTEMS AND THE GREAT LAKES SUBJECT TO THE INFLUENCE OF INDUSTRIAL ACTIVITY. A FOLLOWUP STUDY OF PULP AND PAPER INDUSTRY DISCHARGES WAS RECENTLY COMPLETED.

- BEYOND THE 2,4,5-TCP SITES AND SPECIFIC LOCATIONS WITH FISH CONTAMINATION, 2,3,7,8-TCDD IS NOT A WIDESPREAD CONCERN IN THE ENVIRONMENT.

- EPA, STATES AND OTHER AGENCIES ARE FOLLOWING UP WITH REGULATIONS, HEALTH ADISORIES, TARGETTED STUDIES AND RESEARCH.

The Office of Water, Office of Solid Waste and Emergency Response, and EPA's Regional staff have reviewed and concurred with this report. The report sets forth the overall requirements and the Quality Assurance Project Plan for the National Dioxin Study.

Edwin L. Johnson, Director
Office of Water Regulations
and Standards

Michael Cook, Chairman
Dioxin Management Task Force

Martin Brossman, Quality
Assurance Officer
Office of Water Regulations
and Standards

FOREWORD

This document serves as the Quality Assurance Project Plan of the Environmental Protection Agency's (EPA) National Dioxin Study for study tiers 3, 5, 6, and 7.

The study is part of EPA's Dioxin Strategy (Ref. No. 1) released on December 15, 1983, and is designed to determine the nature of environmental contamination from 2378-TCDD, the most toxic dioxin isomer. This document summarizes the important elements of field and laboratory Quality Assurance and Quality Control (QA/QC) and sets forth the basic objectives of the study. The format of the document is in conformance with the Office of Water (OW) Work/QA Project Plan Guidance document (Ref. No. 2). This document draws upon and provides a bridge between the study's field and laboratory manuals. The laboratory protocol document describes the analytical procedures to be followed and the field sampling document recommends specific field sampling techniques.

This project plan is intended to provide specific guidance to those participating in the National Dioxin Study (EPA Headquarters, Regions, Analytical Support Laboratories, and State Agencies). The plan is designed to help ensure uniformity and an understanding of study objectives so that a valid basis can be established for performing a national assessment.

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. Introduction

Background

On December 15, 1983, EPA released the "Dioxin Strategy" (Ref. No. 1) which provides a framework under which EPA will:

1. study the nature of dioxin contamination and the associated risks to humans and the environment;

2. implement or compel necessary clean-up actions at contaminated sites; and

3. further evaluate regulatory alternatives to prevent future contamination, as well as disposal alternatives to alleviate current problems.

To facilitate the implementation of the strategy, EPA defined the following study tiers based on decreasing potential for 2,3,7,8-tetrachlorodibenzo-p-dioxin (2378-TCDD) contamination:

Tier 1 - 2,4,5-Trichlorophenol (2,4,5-TCP) production sites and associated waste disposal sites.

Tier 2 - Sites (and associated waste disposal sites) where 2,4,5-TCP was used as a precursor to make pesticidal products.

Tier 3 - Sites (and associated waste disposal sites) where 2,4,5-TCP and its derivatives were formulated into pesticidal products.

Tier 4 - Combustion sources.

Tier 5 - Sites where pesticides derived from 2,4,5-TCP have been and are being used on a commercial basis.

Tier 6 - Certain organic chemical and pesticidal manufacturing facilities where improper quality control on certain production processes could have resulted in the inadvertent formation of 2378-TCDD.

Tier 7 - Networks of existing ambient stations where fish and soil will be sampled to determine whether 2378-TCDD is widespread in the environment and, if so, at what levels.

The strategy calls for a complete investigation (including field sampling) at all sites in tiers 1 and 2 because they are suspected of being the most contaminated. A representative sampling of sites in tiers 3 and 6 will be done because the number of sites in these tiers is in the hundreds and the potential for contamination is much less. The work in tier 5 will focus on areas where extensive use of pesticides derived from 2,4,5,-TCP has been documented. The work in tier 7 will use two national networks for sampling ambient conditions.

The initial sampling work at sites in tiers 3-7 constitute the basis of the National Dioxin Study and hence the development

of this project plan covering all tiers except tier 4, which will be covered under a separate project plan being developed by the Office of Air Quality Planning and Standards.

Although the overall objective of the National Dioxin Study is to study the nature of dioxin contamination, sites found to be contaminated at levels of concern with 2378-TCDD will be referred to the Superfund program for any necessary follow-up work.

Implementation

The AA for the Office of Solid Waste and Emergency Response (OSWER) is responsible for implementing the overall dixoin strategy. OSWER will directly manage the investigations for sites in tiers 1 and 2. The Office of Water Regulations and Standards (OWRS) will manage the study of tiers 3 through 7 - the National Dioxin Study. Both efforts will be coordinated by the Dioxin Management Task Force (DMTF). EPA's regional offices will be responsible for conducting the actual sampling for tiers 3, 5, 6, and 7, following the guidelines presented in this document.

A significant portion of this study involves measuring 2378-TCDD in environmental media, especially in soils and fish. Two major laboratory programs will be involved in these analytical determinations: (1) a configuration of three EPA laboratories (Duluth, Bay St. Louis, and RTP) known as the Troika and managed

Office of Research and Development (ORD); and (2) the Contract Lab Program (CLP) managed by OSWER and consisting of commercial laboratories under contract to EPA.

Work in all seven tiers will proceed in a concurrent, parallel fashion. While the basic National Dioxin Study is limited to two years, the comprehensive assessment of sites in tiers 1 and 2 will likely extend beyond two years, especially at sites where enforcement actions and clean-up options are complex.

II. Quality Assurance Project Plan

1.0 Project Name: "National Dioxin Study"

2.0 Project Requested by: U.S. EPA, as a part of EPA's overall Dioxin Strategy in response to a particular request through the Congressional 1984 appropriation

3.0 Date of Request: October 1, 1983

4.0 Date of Project Initiation: October 1, 1983

5.0 Project Officer: Alec McBride, Chief, (202/382-7046) Water Quality Analysis Branch, Monitoring and Data Support Division (WH-553), Office of Water Regulations and Standards, Office of Water, U.S. EPA

6.0 Quality Assurance Officer: Martin Brossman (202/382-7040), Monitoring and Data Support Division (WH-553), Office of Water Regulations and Standards, Office of Water, U.S. EPA.

Project Description

7.1 Basic Approach

There are 75 different chlorinated dioxins, divided into eight homologues (groups), each with different physical and chemical properties depending on the number and location of the chlorine atoms. One of the 22 isomers with four chlorine atoms is 2378-TCDD. This isomer is the principal focus of the National Dioxin Study for three reasons:

(1) it is the most toxic of the chlorinated dioxins,

(2) it is the isomer most often associated with exposure and potential health risks to humans, and

(3) there is sufficient information available on it to allow a targeted study to be developed.

The data reviewed thus far indicate that 2378-TCDD is inadvertently formed during the chemical hydrolysis of tetrachlorobenzene to make 2,4,5-TCP and that it is not formed through any other properly controlled chemical manufacturing process. EPA's scientific judgement is that most of the 2378-TCDD goes into the still bottom wastes from this process, with the remainder contaminating the product. The contaminated 2,4,5-TCP is then used as a precursor to make other chemicals (e.g., 2,4,5-T and silvex) thereby "carrying" the 2378-TCDD contaminant through the chemical manufacturing tree. At each step, chemical measures

can be taken to "clean-up" the product (i.e, remove impurities like 2378-TCDD).

Once the chemical industry learned about the potential for 2378-TCDD contamination, steps were taken to reduce the levels of contamination. These measures typically resulted in lower levels of contamination in both the product and the wastes.

Thus, the characterization of environmental contamination of 2378-TCDD is believed to be two-fold:

(1) A decreasing level of contamination with time from the 2,4,5-TCP chemical manufacturing process, and

(2) a decreasing level of contamination down the chemical tree (i.e., 2,4,5-TCP is more contaminated than 2,4,5-T).

The approach to the National Dioxin Study is based on tiers or categories of contamination; the lower the tier number, the greater the potential for higher levels of 2378-TCDD contamination of both product and wastes. For this reason, all of the facilities involved in making 2,4,5-TCP (tier 1) and 2,4,5-TCP derivatives (tier 2) will be investigated. The investigation in the other production tiers (3 and 6) will be based on a representative sampling of facilities within these tiers because the potential

for significant contamination is low at tier 3 sites and even lower at tier 6 sites.

Sampling at tier 4 will be conducted to determine the presence or absence of 2378-TCDD in combustion sources, both those where material contaminated with 2378-TCDD may have been burned (i.e., municipal incinerators) and those where no 2378-TCDD should have been present in the material being burned (i.e., coal-fired power plants). The latter type of sources will be sampled to investigate the theory that 2378-TCDD can be created in certain combustion processes. As indicated earlier, a separate work plan will be developed for tier 4.

Sampling at tier 5 will be conducted to determine the prevalance of 2378-TCDD at sites known to be sprayed with 2378-TCDD contaminated herbicides.

Tier 7 is being investigated to determine whether 2378-TCDD is widespread in the environment by a representative sampling of fish and soils at control stations, i.e., stations not associated with tiers 1, 2, or 3.

7.2 Project Description by Tiers

7.2.1 TIER 3

Objectives

Tier 3 consists of facilities which formulate pesticides containing active ingredients which may be contaminated with

dioxin. Certain locations within these facilities may have been contaminated with dioxin if the active ingredients of concern were spilled during handling or formulation. Another possible source of contamination would be the cleaning and disposal of containers which had held the active ingredients. Many of the formulators were probably not aware that they were handling material potentially contaminated with dioxin; therefore, they would probably not have taken special precautions for handling and disposing of materials.

The Dioxin Strategy (Ref. No. 1) contends that significant contamination is less likely at tier 3 facilities than at tier 1 and tier 2 facilities. The objective of the tier 3 study is to determine what percentage of the facilities in tier 3 have concentrations of dioxin in soil above one part per billion (ppb) or in other environmental media (e.g., fish in nearby streams) above approximately one part per trillion (ppt). This is a very important question to address since the answer will provide the Agency with an indication of what, if anything, should be done about the hundreds of tier 3 facilities which are not being sampled as part of the National Dioxin Study. This determination will be based on sampling within each site in a manner which, where possible, is directed towards those specific locations within a site that are most likely to be contaminated. The study will not be able to statistically compare contamination levels

across facilities since the field sampling at each tier 3 site will be conducted based upon the characteristics of that particular site.

The Agency does have information on production for many tier 3 facilities and will be collecting additional data from questionnaires sent to all of the facilities in this tier. It is possible that these data will allow EPA to characterize contaminated and uncontaminated facilities in terms of certain variables. Hopefully, these characterizations will assist in directing any further investigations beyond the national study which may be necessary for tier 3.

Implementation

The methodology used to accomplish these objective includes: 1) identifying formulated compounds containing 2,4,5-TCP and/or its derivatives, 2) identifying facilities that use these compounds in pesticide formulation, 3) selecting an appropriate number of facilities to sample so that results can be statistically extrapolated to all other facilities in tier 3, 4) identifying which locations to sample at each facility, 5) determining the type of samples to be collected (soils, fish, etc.), and 6) determining whether additional facilities should be selected for dioxin sampling.

Six additional pesticide formulation compounds have been identified to contain 2,4,5-TCP and/or its derivatives. They are 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), silvex, erbon, ronnel, hexachlorophene, and isobac 20. EPA has identified 583 facilities that potentially used these compounds or 2,4,5-TCP itself in the formulation of pesticide products:

- o 258 facilities were identified from the FIFRA and TSCA Enforcement System (FATES) which provides production levels for each facility for the years 1976-1981.

- o 325 facilities were identified from four other data sources: (1) the Office of Pesticide Programs Registration file, (2) a report entitled Dioxins (Ref. No. 3), (3) regional recommendations, and (4) those originally identified in tiers 1 and 2 but which were found to be formulation rather than production facilities of 2,4,5-T and its derivatives.

Fifty facilities were statistically selected for the initial sampling program from the FATES database of 258 such that an extrapolation could be made to all the pesticide formulators listed in FATES. If 10 percent of the facilities in tier 3 are found contaminated, then the 95 percent confidence interval for the percentage of all contaminated facilities in the FATES

database is between two and 18 percent. Large production facilities were statistically represented in the sampling program by first ranking facilities according to production and then selecting a statistical sample of six facilities from the 31 largest. The remaining 44 facilities were selected based on regional distribution. This was accomplished by stratifying the facilities into six clusters and selecting an appropriate number based on calculated sampling weights for each cluster.

An additional 37 facilities were identified by the regions as being of particular interest and are also included in the initial sampling program. The results from these 37 facilities will not, however, be used in the extrapolation since they were not randomly selected.

The regional offices sent information request letters under CERCLA authority to each of the 87 facilities to be sampled to verify existing EPA records as well as to obtain additional information (e.g. quantities of waste generated, the disposal method, and location of disposal sites). A sampling plan will be developed by the regional offices for each site based upon the results of these information request letters and on reconnaisance site visits.

Site-specific sampling plans will identify the locations within each facility to sample, focusing on areas most likely to be potentially contaminated with dioxin. These areas would

include areas where potential spillage and leakage occurs (e.g. loading/unloading areas, storage areas, disposal areas, and stormwater drainage areas). The reason for following a directed sampling plan as opposed to a random one is the belief that only a small portion of a site is likely to be contaminated and that one can make a reasonable judgement as to where that portion of the site is located. However, using a directed approach does preclude the ability to extrapolate to all of the facilities the levels of contamination found at the different sites.

At sites where the information is inadequate to establish a directed sampling plan or where additional coverage is desired in conjunction with directed sampling, a random sampling scheme should be developed as described in Section 12 of this document.

EPA also intends to obtain the Office of Management and Budget's (OMB) approval for a questionnaire to be sent to tier 3 facilities not included in the initial 87 to be sampled as well as to any other facilities identified by the Department of Defense as Agent Orange formulators. Responses to these questionnaires will be evaluated to determine if another list of candidate facilities should be created, from which a second set of tier 3 facilities may be selected for investigation. Our initial hypothesis is that most of the facilities not listed in the FATES database may have registered to handle one of the pesticides of

concern but never actually handled the pesticides. The questionnaire responses will be used to evaluate the hypothesis. The Agency has not made any provisions for verifying the validity of the questionnaire responses.

The tier 3 investigation focuses only on formulation facilities and does not follow products through the distribution system (i.e., warehouses, retailers, storerooms of commercial applicators) because of the lower potential for contamination and the limited resources.

7.2.2 TIER 5

Objectives

Tier 5 consists of those areas where pesticides derived from 2,4,5-TCP were used or are being used. Ideally, an investigation for tier 5 would be designed to: 1) initially identify all uses and areas of potential pesticide use for all seven products of concern; 2) conduct a detailed investigation identifying all actual use areas and amounts used; and 3) select a probability sample of sites from the pesticide use population. From this type of study a determination could then be made identifying which particular uses result in detectable levels of dioxin, and subsequently, which uses might represent a human health risk.

However, the available information on uses of these pesticides is neither comprehensive nor detailed enough to allow this type of

approach. Therefore, the tier 5 study will focus on those areas where extensive use of the pesticides 2,4,5-T and silvex has been documented. The rationale for limiting the scope to these pesticides is that, based on preliminary information from the Office of Pesticide Programs, these pesticides have been more heavily used and have a greater potential for human exposure than the other five pesticides which are of lesser interest due to: (1) low levels of active ingredient pesticide in the end-products, (2) lack of use documentation, (3) use on very small areas, or (4) a wide diversity of uses at low levels of application. The study may include sampling at 2,4,5-TCP use sites (such as leather tanneries or wood preserving facilities) if adequate information can be developed on specific facilities which used this compound as a pesticide.

Implementation

Candidate sites for investigation were compiled by headquarters and regional personnel working in conjunction with state or local agencies. Selected sites include ones where the major continuing and/or extensive past use of 2,4,5-T and silvex have been documented (i.e., rice fields, sugarcane fields, rangelands, forests, rights-of-way, and recreational areas). The selected sites will be sampled to get a general characterization of each major use and will serve to determine if further investigation of a particular use is required.

Media to be sampled will include soils, stream sediments, fish tissue, vegetation, animal tissue, and/or any other appropriate media as determined by the responsible regional office. Sampling location and methods will follow the detailed protocols in the field guidance manual. Priority will be given to soil and sediment sampling since dioxin applied to an area by pesticide use will most likely reside in these media as a result of dioxin transport and fate processes (Ref. No. 4).

The number of soil samples to be collected will be between 24 and 48 discrete samples randomly distributed at each of approximately 20 tier 5 sites (see Section 12 of this document). These samples will be analyzed at the ppt level of detection. This approach results in a 70 - 90 percent level of confidence that dioxin will be detected if it is present at five percent of the area within the site. This approach assumes that one cannot identify "hot spots" within a site and that there is either a uniform or a random distribution of dioxin within the site. This assumption is based on the application methods for 2,4,5-T or silvex. Sampling plans will be developed by the regional offices for each of the tier 5 sites.

7.2.3 Tier 6

Objectives

Tier 6 consists of selected organic and pesticide manufacturing facilities where, under unusual or poorly controlled operating conditions, dioxin may have been created. The objectives for the tier 6 study are identical to those for tier 3; that is to determine the percentage of facilities which are contaminated at levels of concern and where possible, to characterize those facilities in terms of production variables.

Implementation

The methodology used to accomplish this objective includes: 1) identifying those commercially significant organic and pesticide compounds where improper quality control on production processes could result in the formation of 2378-TCDD contaminated products, 2) identifying facilities that manufacture these compounds, 3) selecting an appropriate number of facilities so that results can be statistically extrapolated to other facilities, 4) identifying locations to sample at each facility, 5) determining the type of samples to be collected (soils, fish, etc.), and 6) determining whether additional facilities should be selected for dioxin sampling.

Dioxins (Ref. No. 3) identified organic and pesticide compounds (totaling 125) whose production could inadvertently create

dioxin based on their molecular structure, process sequence and commercial significance. The production of only 60 of these compounds could potentially lead to 2378-TCDD formation. Dioxins (Ref. No. 3) defined commercially significant products as those produced in quantities in excess of 1,000 pounds per year and/or wholesales reaching $1,000 per year. Most of the organic chemicals identified are used as manufacturing intermediates.

EPA identified 60 facilities that manufacture these 60 compounds using four sources of information: (1) the SRI Directory of Chemical Producers (1977-1983), (2) FIFRA and TSCA Enforcement System (FATES), (3) the Dioxins report (Ref. No. 3), and (4) regional suggestions.

Nineteen facilities were statistically selected for the initial sampling program based on regional distribution so that extrapolation could be made to all these manufacturing facilities. This selection was accomplished by stratifying the facilities into five clusters and selecting an appropriate number based on calculated sampling weights for each cluster. If 10 percent of facilities in tier 6 are found contaminated, then the 95 percent confidence interval for all contaminated tier 6 facilities is between three and 23 percent.

Information collection and field sampling procedures (including the number and allocation of soil samples) for tier 6 facilities

will be identical for those used for tier 3 facilities. Particular attention will be given to reported production levels, which for the organics are not currently available. Sampling plans will be developed by the regional offices for each of the tier 6 sites.

Tier 6 focuses only on production facilities as a potential source of dioxin release into the environment. The potential for dioxin contamination from these products at distribution facilities (i.e. warehouses, applicators and retail stores) is not expected to be significant and sampling at these facilities is not included as part of this tier.

7.2.4 TIER 7

Objectives

Tier 7 consists of areas other than those where known or suspected sources of 2378-TCDD contamination are located. The basic goal of the tier 7 study is to evaluate the extent and severity of 2378-TCDD contamination in the environment. In addressing this goal, the study will focus on contamination of soil and fish tissue since these are the media which present the greatest potential exposure to humans. Also, 2378-TCDD tends to adsorb strongly to soil particles and to bioaccumulate in fish tissue.

Specific objectives of the tier 7 study are to: 1) determine the percentage of sites in the EPA Urban and Rural Soil Networks which have measurable levels of 2378-TCDD in soil and 2) determine

the percentage of sites in the U.S. Geological Survey's National Stream Quality Accounting Network (NASQAN) which have measurable levels of 2378-TCDD in fish tissue. If 2378-TCDD is detected at a significant number of locations (approximately 20 percent or more), the Agency will attempt to determine what typical "background" levels are and whether they are related to specific variables describing the different sites. All tier 7 analyses - both for fish and soil - will be done at approximately the ppt level of detection.

Implementation

Tier 7 consists of two phases: 1) a soil sampling survey, and 2) a fish screening survey. Soils were selected for sampling since dioxin reaching the soil will be strongly sorbed; biodegradability, plant uptake, and leaching are not believed to be important fate processes (Ref. No. 3). Photodegradation is limited to a near-surface phenomenon, and dioxin transport in many cases is due to erosion of contaminated soil which is transported to the water environment. Dioxin is thought to enter the atmosphere adsorbed to particulates, and that which is not photodegraded is subsequently deposited. As a result of these fate processes, soil is an appropriate and informative medium to sample in determining background levels of dioxin.

Soil sampling will be accomplished through use of the Office of Pesticides Program National Soils Monitoring Program (NSMP).

The objectives of this program are to monitor for the presence of pesticide residues in urban and rural soils and to determine trends of levels through time (RTI; Ref. No. 5). (Refer to the National Soil Monitoring Program (RTI; Ref. No. 5) and Urban Soils Monitoring Program (RTI; Ref. No. 6) for a complete description of the network designs.) The rural network consists of over 13,000 sites and is a valid probability sample of sites from the 1967 Conservation Needs Inventory (CNI) of rural land areas in the conterminous United States. Sample design and site identification have already been done. For tier 7 sample selection, the network has been ordered by EPA regions and states. Five systematic samples of equal size (40) were randomly selected to yield 200 sample sites from which various estimates of soil contamination can be made describing the population of soils of the rural network. If 10 percent of the sites are found contaminated, then the 95 percent confidence interval for all contaminated sites in the network is between seven and 13 percent.

Although the rural network is a valid subsample of the CNI, no valid structure exists to provide the basis for analyzing the CNI, and therefore, the rural network data, except through artificial methods. Other restrictions in using the rural network are: 1) sample numbers vary considerably from state to state such that reliable estimates of average levels will not be available for some geographic areas and 2) the CNI database is 17 years old, and a number of locations may have changed characteristics.

Three hundred soil sites have been selected from the 20 Standard Statistical Metropolitan Areas (SMSAs) monitored in the urban soil network. If 10 percent of the sites are found contaminated, then the 95 percent confidence interval for all contaminated sites in the network is between eight and 12 percent. SMSAs were ordered by EPA regions and states, and five random systematic samples of 60 sites each were selected. In addition to the selected sites, soil samples may be taken at one industrial site in each SMSA; these sites will be selected by regional personnel. Sampling will follow protocols summarized in Section 12 of this document and detailed in the field guidance manual.

Fish are known to bioaccumulate many compounds, including dioxin, to much higher levels than surrounding waters. In addition, fish represent a direct route for human uptake via ingestion. In estuarine and coastal areas, mussels or oysters will be collected to determine background levels. Similar to fish, shellfish are known bioaccumulators and represent a direct route for human exposure through consumption. Although depuration tends to be more rapid in shellfish than in finfish, the migratory behavior of most marine fish may not reflect the actual conditions of the collection site, thereby making shellfish preferred specimens to collect to meet tier 7 objectives in coastal areas. As with soils, sampling will follow procedures summarized in Section 12 of this document and detailed in the field guidance manual.

Sampling protocols call for collecting specimens of bottom-feeding and game fishes in freshwaters and mussels or oysters in estuarine and coastal waters. Methods specified serve to limit variables reducing the difficulty in interpreting the data. These include establishing target species (to reduce interspecies variations), sampling fish of similar age where possible, and limiting time of sampling to reduce seasonally-related differences (e.g., lipid content). Composite samples of whole bottom-feeding fish, whole game or commercial fish, bottom-feeding fish fillets, and game or commercial fish fillets will be collected. The bottom-feeding whole fish composite will be analyzed first, and if contamination is detected, the other samples will then be analyzed.

As in the case of the soils survey for tier 7, sample design for fish sampling also utilizes existing monitoring networks - specifically the U.S. Geological Survey's National Stream Quality Accounting Network and Benchmark Network. One hundred stations were statistically selected so that the results could be extrapolated to the combined networks. If 10 percent of the sites are found contaminated, then the 95 percent confidence interval for all contaminated sites in the network is between five and 15 percent. Replicate samples will be collected at 25 of these sites in order to estimate the variability at a site. In addition, approximately 315 sites were selected from the networks and from

additional locations of regional or national interest. These additional sites represent locations of interest because of nearby population centers, commercial or recreational fishing activity, and availablity of relevant water quality information.

7.3 Monitoring Parameters and Their Frequency of Collection

1. 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2378-TCDD).

This parameter will be measured in all samples which are collected as part of the study. Media collected will include wastewater, surface water, groundwater, sediment, soil, aquatic organisms, and terrestrial specimens. The frequency of collection will be defined in the individual regional site-specific plans. It is estimated that samples will be analyzed at the rate of 100 to 150 per month using the EPA Analytical Troika; the rate using the CLP will be somewhat higher. All samples analyzed by the Troika will be retained for possible further analytical work.

2. Polychlorinated Dibenzo-p-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs).

The extent and frequency of these measurements have not been determined. The following groups of isomers are being considered:

Group	Number of Isomers
Tetrachlorodibenzo-p-dioxin	22*
Pentachlorodibenzo-p-dioxin	14
Hexachlorodibenzo-p-dioxin	10
Heptachlorodibenzo-p-dioxin	2
Octachlorodibenzo-p-dioxin	1
Tetrachlorodibenzofuran	38
Pentachlorodibenzofuran	28
Hexachlorodibenzofuran	16
Heptachlorodibenzofuran	4
Octachlorodibenzofuran	1

* Includes 2378-TCDD

The identification of specific isomers within each group depends on the availability of analytical standards and the ability of the selected chromatography columns to resolve isomers. Most determinations will be non-isomer specific (i.e., total tetrachlorodibenzofurans, etc.) and semiquantitative (because analytical standards are not available, the concentrations are estimates).

3. Percent Lipids

The lipid content of each contaminated fish and a representative subsample of uncontaminated fish will be determined.

4. Percent Moisture

The moisture content of all soils and sediments measured at the ppt level will be determined by Troika; the results will be reported on a dry weight basis. The moisture content will not be determined for soils measured at the ppb level by the CLP. The results will be reported on a net weight basis.

5. Fish Aging

ERL-Duluth will remove and store scale and otolith specimens of each whole bottom-feeding fish sample. Depending on the levels of dioxin found and the percentage of fish found contaminated, OWRS will decide if fish age will be estimated. If aging is necessary, each contaminated fish and a representative subsample of uncontaminated fish will be aged.

6. Determination of weight, size, and species of aquatic organisms and terrestial animals.

Each region will have the responsibility for determining the weight, size, and species for all aquatic organisms and terrestrial animals.

A summary of the parameters discussed is shown in Table 1.

TABLE 1 - PARAMETER TABLE

Parameter	Number of Samples (Estimate)	Sample Matrix*	Method Reference	Sample Preservation	Holding Time
2,3,7,8-TCDD	Unknown	Water	7	4°C/Dark	7 days - Extraction 40 days - Analysis
2,3,7,8-TCDD	3800-7400	Soil/Sediment	7,8	4°C/Dark	Indefinite
2,3,7,8-TCDD	600	Fish	7	Freeze/Dark	Indefinite
PCDDs/PCDFs	Unknown	All	7	Same as for TCDD	Same as for TCDD
Lipid	Unknown	Fish	7	Freeze/Dark	(Undetermined)
Moisture	980-1460	Soil/Sediment	7	4°C/Dark	(To be performed at time of chemical analyses)
Speciation/ Weight/Size	600	Fish	9	None	Indefinite
Aging	Unknown	Fish	9	Freeze/Dark	Indefinite

* Plant and animal tissue will also be evaluated on a site and issue specific basis.

8.0 Financial Information

The following resources have been earmarked for the National Dioxin Study. They are funded in the Water Quality Monitoring and Analysis program element (53B2F) of EPA's budget.

	Current Operating Plan FY 1984		President's Budget Request FY 1985	
	FTE	AC&C $(000)	FTE	AC&C $(000)
Headquarters			[a]	[e,f]
OWRS (Program office) (AH28)		385.0	5.5	3400.0
ORD/OEPER (Troika) (AH63)		835.0		
ORD/OMTS (Troika) (AH60)		50.0		
OPP (Troika) (AH32)		350.0		
Agency reserved (AH92)		165.0		
OAQPS (Tier 4 work) (AH53)		715.0		
Hqs Total	0	2500.0	5.5	3400.0
Regions				
Region 1	1.0	75.0	1.0	
2	1.0	175.0	1.0	
3	1.0	125.0	1.0	
4	1.4	200.0	1.4	
5	1.4	250.0	1.4	
6	1.3	200.0	1.3	
7	1.4	200.0	1.4	
8	.5	75.0	.5	
9	.5	100.0	.5	
10	.5	100.0	.5	
Reg. Total	10.0 [b]	1500.0	10.0 [b]	0
Total EPA	10.0 [c]	4000.0	15.5	3400.0

Footnotes:

a Sources of Headquarters FTE estimates are: FY84 -- EPA's Budget Request to OMB for FY85 (Form BUD-2), September 1983. FY85 -- OWRS Budget Plans, February 27, 1984.

b Source of Regional FTE estimates is Regional Workload Model for Water Quality Monitoring and Analysis, February 16, 1984.

c Note that many EPA offices are contributing efforts toward the National Dioxin Study which are not reflected in these estimates, since these estimates were made prior to actual initiation of the study.

d $165,000 is being held in Agency reserve in exchange for $165,000 in Salaries and Expenses funds allocated by the Comptroller's office to:

OPP	(AH32)	139,000
OEPER	(AH63)	26,000

e In addition to the $3.4 million, OW has earmarked $250,000 for study of persistent and bioaccumulative pollutants in the FY85 President's Budget request.

f Some portion of these funds will be allocated to other Headquarters offices and to the Regions in FY85.

Abbreviations:

AC&C Abatement Control and Compliances appropriation, commonly referred to as "extramural."

AH Allowance Holder number.

FTE "Full Time Equivalent" employees.

9.0 Schedule of Tasks and Projects

The major items needed for completion of the National Dioxin Study for tiers 3, 5, 6, and 7 are:

1. Overall regional plan will be prepared and will include: a brief organizational section; information on how the region

will arrange sampling in each of the tiers; a plan for using all extramural funds; and a tentative schedule for sampling. These plans were due by June 1, 1984.

2. Site-specific sampling plans will be prepared by each region. These plans will include: information on sampling site location (including latitude/longitude); site sampling plan with discussion of rationale; and site-specific safety and community relations issues. These plans will be submitted to OWRS for review prior to sampling.

3. Review and approval of site-specific plans occurs before the region does any sampling at a site.

4. Samples are collected and shipped over a period of time arranged with the Sample Control Center and Sample Management Office consistent with Troika and CLP capacity to meet holding times specified in Table 1.

5. All National Dioxin Study sites for tiers 3, 5, 6, and 7 are finalized prior to site-specific plan submittal deadline.

6. A certification and audit program for Contract Labs has been developed and implemented by EMSL-LV for ppb soil analyses.

7. In December, 1984, OWRS will prepare an interim report describing the status of the study and presenting any results available at that time.

8. OWRS will prepare a final report on the results of the study by December, 1985.

10.0 Project Organization and Responsibility

The following is a list of key study personnel and their corresponding responsibilities.

National Dioxin Study responsibility: Edwin L. Johnson
Director, OWRS

Dioxin Management Task Force Chairman: Michael Cook, OSWER

Project Director: Alec McBride, OWRS/MDSD

Assistant Project Director: Stephen Kroner, OWRS/MDSD

Troika Laboratory Director: Norbert Jaworski, ERL, Duluth

Contract Laboratory Coordination: Stan Kovell, OSWER

Field Sampling Plan Review: Stephen Kroner, OWRS/MDSD

Quality Assurance Officer: Martin W. Brossman, OWRS

Quality Assurance Task Group: Martin Brossman, OWRS/OW
Richard Spear, Region II
Gerald McKenna, Region II
James Adams, Region V
Marsha Kuehl, Region V
Charles Hensley, Region VII
Robert Kleopfer, Region VII
Michael Dellarco, QAMS/ORD

Data Management: Alec McBride (STORET)

Laboratory Audit Team (Troika): Two or three members to be designated by the Quality Assurance Task Group

Field Audit Team: Regional QAO with selected support

Data Review and Validation (Total): Alec McBride

Peer Review (Concepts and Reports): To be determined by the Dioxin Management Task Force

National Dioxin Study Regional Coordinators -

Region I	-	Bill Walsh
Region II	-	Rick Spear
Region III	-	John Ruggero
Region IV	-	Rebecca Slack
Region V	-	Howard Zar
Region VI	-	Dave Parrish
Region VII	-	Billy Fairless
Region VIII	-	Bill Geise
Region IX	-	Kathleen Shimmin
Region X	-	Anita Frankel

11.0 Data Quality Requirements and Assessments

Table 2 summarizes the expected quality of the data in terms of precision, accuracy, and detection limits. Specific details are given in the individual analytical procedures (Ref. Nos. 7 & 8). For purposes of controlling data quality, a sample set consists of the following:

TROIKA	CLP
12 Environmental Samples[a]	21 Environmental Samples[a]
1 Matrix Spike[d]	1 Matrix Spike[b]
1 Performance Sample[e]	1 Performance Sample[c]
1 Method Blank[d]	1 Method Blank[d]
1 Field Blank[e]	1 Field Blank[e]

a = Including any field replicates needed
b = Provided by Regions through SMO
c = Provided by SMO (through EMSL-LV)
d = Responsibility of laboratory
e = Provided by Regions (through Headquarters) for soils

The data quality of a given set of samples is assessed in relation to the following criteria:

1. Daily verification of isomer specificity.
2. Daily verification of response factor.
3. Qualitative criteria (isotope ratios and retention times) for all positives.
4. All field blanks and method blanks must be free of any detectable TCDD.
5. Performance sample must meet criteria (See Table 2).
6. Spiked sample must meet criteria (See Table 2).
7. For the CLP, the surrogate must be measured to $\pm$ 40 percent in every sample; for the Troika, the internal standard must be recovered to $\pm$ 30 percent.
8. For the Troika effort, one complete set will be split with a contract lab on a quarterly schedule. The specific samples will be selected by Troika.

TABLE 2

Summary of Quality Control Targets for 2378-TCDD Measurements

Matrix/Lab	Target Detection Limit	Bias[a]	Precision[b]
Soil/CLP	1.0 ppb	±25%	≤25%
Ambient Water/TROIKA[c]	0.03-.1 ppt	±30%	≤30% if >6 D.L. ≤100% if ≤ 6 D.L.
Soil/TROIKA	1 - 10 ppt	±30%	≤30% if >6 D.L. ≤100% if ≤ 6 D.L.
Fish/TROIKA	1 - 5 ppt	±30%	≤30% if >6 D.L. ≤100% if ≤6 D.L.
Animal Tissue/TROIKA	1 - 5 ppt	±30%	≤30% if >6 D.L. ≤100% if ≤6 D.L.
Plants/TROIKA	5 ppt	±30%	≤30% if >6 D.L. ≤100% if ≤6 D.L.
Wastewater/TROIKA	5 ppt	±30%	≤30% if >6 D.L. ≤100% if ≤6 D.L.

ppb = parts per billion

ppt = parts per trillion

(a) As determined from in lab matrix spikes and expressed as a percent.

(b) As determined from within lab replicates and expressed as relative standard deviation.

(c) All TROIKA targets are subject to revision as additional analytical work is completed.

11.1 Data Comparability

Measures taken to ensure comparability of analytical work performed by different laboratories include the following:

- Standardized written sampling and analytical procedures.
- Standardized field and compatable analytical data forms, sample identification tags, and chain-of-custody records.
- All CLP laboratories will use the same certified standard solution of 2378-TCDD as provided by EMSL-Las Vegas for preparation of all calibration standards. The Troika labs will use a primary analytical standard which has been referenced to the EMSL-Las Vegas standard as well as other verified standards.
- All laboratories will be provided with performance evaluation samples on a regular basis.
- Standard handling and shipping procedures will be used for all collected samples.
- Replicate analyses will be done on samples in order to evaluate both within and between-laboratory precision.
- A uniform supply of sampling containers will be utilized.

- The results for performance evaluation samples and inter-laboratory duplicate analyses will be the primary means for verifying the comparability of data within a single laboratory. The Troika QC results will also be used to evaluate method performance.

11.2 Data Representativeness

See Sections 7.0 and 12.0 for a discussion of data representativeness for each tier.

11.3 Data Completeness

The target for completeness of the data in order to meet the project needs is 80%, and the measure to be used in meeting this target is the percent of total reported data classified as valid in the data validation process.

12.0 Sampling Procedures

12.1 Tiers 3 & 6

At most facilities the majority, if not all, samples taken will be soil samples. Where there is a water body near the facility, stream sediment and/or fish tissue samples may be taken. Regional personnel will make the determination as to whether samples taken from drainage ditches should be treated as soil samples or sediment samples. A discussion for sampling sediments

locations more likely to be contaminated, it may decide to follow a random sampling approach for the entire site.

A random sampling approach consists initially of dividing the facility area into equal size grids with dimensions not exceeding 50 feet by 50 feet. Samples are collected within randomly selected grids (directly in the center of the grid). Grids that are covered by buildings are excluded from the random selection process. For a site which is sampled in a completely random manner, if five percent of the site is contaminated, this sampling approach provides a 70 percent confidence level of detecting contamination with 24 samples and a 90 percent confidence level of detecting contamination with 48 samples.

12.2 Tier 5

Although sampling at tier 5 sites may include several environmental media, priority will be given to soil and sediment sampling since dioxin applied to an area by pesticide use will most likely reside in these media.

Discrete soil samples will be collected using identical methods as in tier 3. Also, appropriate standard reference soils will be supplied by OWRS and included in each sample set (as defined under Section 11.0) for shipment to the laboratory.

Specific sampling methodologies for sediments depend on the nature of material to be collected, depth of water above the

sediment, sampling location, and equipment availability. Methods will be determined by responsible regional personnel.

While sampling sediments for 2378-TCDD, it is important not to disturb the top layers of sediment and to minimize loss during sampling. Therefore, scoops and drag buckets are not considered for use as sampling devices. In wadeable waters, the direct use of a Teflon core liner is preferred. Core liners can serve as sample containers for shipment, thereby eliminating the need for time consuming extrusions in the field. In waters of greater depth, Ekman or Ponar grab samples are preferred. After retrieval, the sample is to be subsampled with Teflon coring tubes. In terms of volume, 500 grams of sediment is the minimum sample mass to be collected. Sample handling, preservation, and transport are to follow the protocols set forth in the sampling guidance manual.

The number of soil and/or sediment samples to be collected at each site will be between 24 and 48, and the sample collection locations will be identified following the random sampling approach described for tier 3 and 6 sites. Sediment samples will be collected along equally - spaced points on sampling transects.

12.3 Tier 7

Fish samples (both bottom-feeders and game fish) are to be taken at freshwater sites; shellfish samples only are to be taken at estuarine and marine sites.

Enough fish of the same species are to be collected at each site to allow for a minimum sample mass of 500 grams for each of the following four separate samples: one composite of whole bottom-feeding fish, one composite of bottom-feeding fish fillet, one composite of whole game fish, and one composite of game fish fillet. All filleting with be done in the laboratory, and skins will be removed.

Target species have been established to reduce interspecies variability. Target species for bottom-feeding fish, in order of perference are: Carp (Cyprinus carpio)

White sucker (Catastomus commersoni)

Channel catfish (Ictalurus punctatus)

Target species suggested for game fish are:

(a) Cold water stations: rainbow trout (Salmo gairdneri), brown trout (S. trutta), brook trout (Salvelinus fontinalis), lake trout (S. namaycush);

(b) Warm water stations: largemouth bass (Micropterus salmoides), or other members of the sunfish family (e.g., Pomoxis sp.), bluegill (Lepomis macrochirus), etc.

(c) Cool water stations: walleye (Stizostedion vitreum) or other members of the perch family.

Collection of fish specimens of similar age class (two or greater) and limiting collection to non-spawning periods (such as early fall) are required to reduce seasonally-related differences. Each fish is to be wrapped in foil and placed in a plastic bag and properly labeled for type of analysis (whole or fillet).

Target species for estuarine and marine sites are the bivalves Crassostrea virginica (Eastern oyster), Mytilus californianus and M. edulis (commom blue mussel). The minimum sample mass (per species) is 500 grams of tissue (excluding shell). Bivalves should be individually wrapped in foil and placed in a plastic bag for each site.

Specific sampling methodologies for fish and shellfish depend primarily on water conditions, target species for collection, and avaliable equipment. Methods will be determined by appropriate regional and field personnel. Regardless of the method employed, a rapid collection technique is to be employed as not to cause prolonged stress on the organism; in most cases, therefore, active collection techniques are preferred.

Soil collection techniques at rural and urban sites are identical to those previously described for tier 3 (e.g., tulip bulb planter, four-inch deep core, 50' x 50' grid, number of performance samples and field blanks, etc.). At designated sampling sites for urban sampling, one discrete sample will be taken at the mid-point of the site. At designated rural 10-acre sites, the area will be divided into equal sized grids from which one will be randomly selected. One discrete soil sample will be collected at the mid-point of the grid.

Sample handling, preservation, and transport are to follow the protocols set forth in the sampling guidance manual.

13.0 Sample Custody Procedures

Sample Control procedures will be in strict conformance with those procedures provided in the Sampling Guidance Manual for the National Dioxin Study (Ref. No. 9). Figure 1 is a flow chart of sample control to be used in the study.

NEIC chain of custory procedures will be followed for all tiers of the National Dioxin Study. Required chain of custody forms will be provided through the regional study coordinators.

14.0 Calibration Procedures and Preventive Maintenance

Calibration and maintenance of field equipment is contained in the Sampling Guidance Manual for the National Dioxin Study

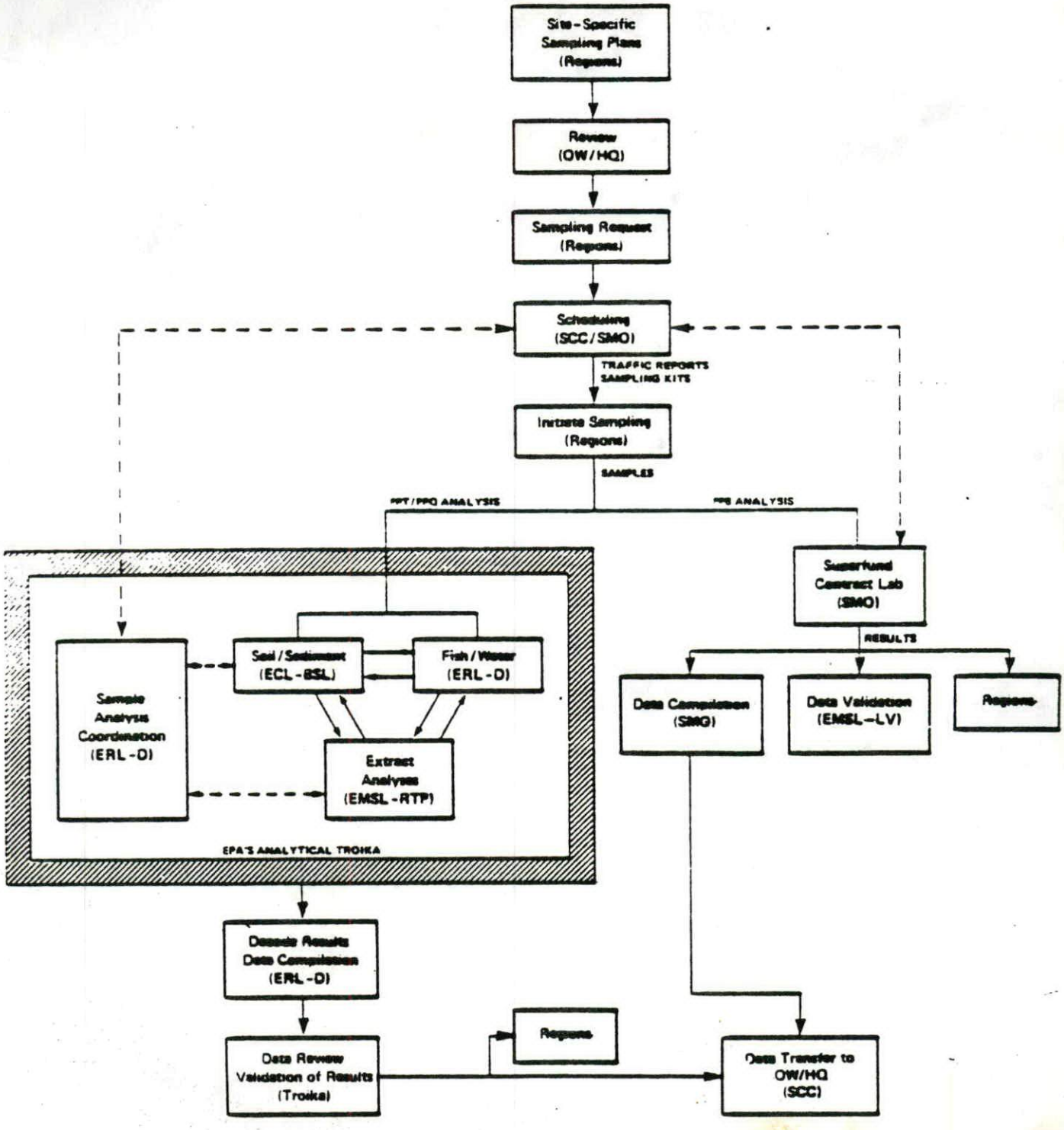

Figure 1 – NATIONAL DIOXIN STUDY, TIERS 1 THROUGH 7 – SAMPLE COLLECTION AND ANALYSIS

(Ref. No. 9). Analytical instrumentation calibration and maintenance procedures are included as part of the Analytical Procedures and Quality Assurance Plan for the National Dioxin Study (Ref. No. 7).

In addition to the referenced SOP's above, each site sampled should be documented in a bound field logbook. This logbook should delineate the exact type and frequencey of field equipment calibration, cleaning and maintenance. All repairs made during the course of the sampling should also be noted. Specific model or serial numbers of all equipment used should be listed, along with the lot or batch numbers of all reagents used to treat or clean any equipment in contact with the samples.

15.0 Documentation, Data Reduction, and Reporting

Documentation, data reduction, and reporting will be in strict conformance with the protocols specified in references 7 and 8. All data will be entered into the STORET system. The data quality will be described in quarterly reports prepared by the Water Quality Analysis Branch.

16.0 Validation

Data will be validated according to procedures specified in references 7 and 8. The data will be coded either valid or invalid depending on adherence to the specified quality control criteria. The CLP data is anticipated to be reviewed and vali-

dated by EMSL-LV, concurrent with reporting to the regions. The Troika data will be reviewed and validated internally (by Troika) and also independently (by contractor) prior to reporting to the regions. The regions are responsible for reviewing the data for reasonableness based on a knowledge of the site characteristics and the specific locations of individual samples. Any disagreements between the reporting lab and the regional reviews will be resolved by the Quality Assurance Task Force.

17.0 Performance and System Audits

Throughout the National Dioxin Study, audits will be conducted by EPA personnel.

17.1 System Audits

The systems audit consists of an on-site visit to contractor analytical labs by EMSL-LV for the purpose of evaluating laboratory operations and quality control procedures. These site visits to contract laboratories should be made prior to the reception of samples, and periodically during active analytical work. EMSL-LV (Ref. No. 8) provides the Standard Operation Procedure to be used for the on-site laboratory evaluations.

An audit team consisting of 2 to 3 persons designated by the Quality Assurance Task Force, including a representative from EMSL-LV, will perform on-site audits of the three Troika laboratories to assess the laboratory operations in regard to implementation

of this quality assurance plan. These audits will be performed at least once a year.

The regional QAO and selected support will perform field audits at least once a year.

17.2 Performance Audits

Performance audits will consist of the analysis of performance evaluation samples supplied to contract laboratories, and in the evaluation of the corresponding analytical results by EMSL-LV. Initially, the laboratory must demonstrate their ability to analyze for 2378-TCDD. EPA will provide to each analytical laboratory two or more performance evaluation samples. Results of these performance evaluation samples must be determined to be within acceptable limits before a laboratory is permitted to analyze any samples. Contracted laboratories will be required to analyze performance evaluation samples on a periodic basis as a continuing check on performance.

The Troika will also analyze performance evaluation samples with each set of samples. In addition, once per quarter, Troika will select a complete set of samples to be analyzed by a qualified independent lab approved by EMSL-Las Vegas. The results will be statistically compared by the QA Task Group based or guidance from QAMS, and any significant differences will be resolved before other analyses are resumed.

17.3 Deficiencies

Any deficiencies or unacceptable performance noted in the audits will be relayed immediately to the persons responsible. A deadline for a plan of corrective action and its successful completion will be given. Documentation of corrective action will be required in the form of a follow-up on-site audit or performance evaluation sample.

18.0 Corrective Action

Identifying, correcting, and documenting quality control problems are the most crucial parts of a Quality Assurance Project Plan. Two systems for dealing with corrective action are needed. The technical or analytical trigger points for corrective action are defined in the "Analytical Protocols and Quality Assurance for the National Dioxin Study" (Ref. No. 7). Administrative quality control lapses require a different scheme.

Three operational areas of the plan could trigger the need for corrective action initiating from the administrative level: field sample collection, document control, and the data validation processes. When a "defect" or deviation from the QA Project Plan occurs in one of these areas, the following actions and documentation must occur:

1. Responsible person for the problem area as outlined in Project Organization and Responsibility must document the deviation/defect discovered.

2. This documentation must include:

- Date and time deviation/defect noted
- Date deviation/defect documented
- Suspected cause of deviation/defect
- Proposed sequence of action to correct defect
- Person(s) responsible for carrying out corrective action
- Date action completed
- Follow-up dates on effectiveness of action
- Final approval of action by responsible person

3. All such documented deviations/defects should be readily accessible to the on-site audit teams to verify that an effective and timely corrective action system is operational.

19.0 Reports

A series of reports and documents have been prepared which provide background information and on-going guidance for the National Dioxin Study.

The Dioxin Strategy published on November 28, 1983, covers the total agency effort on dioxin including the National Dioxin Study.

The National Dioxin Study Work Plan of January 15, 1984 (Ref. No. 11), assigned to the regions the responsibility for developing sampling plans. The work plan included a tentative list of sites to be studied and underwent revision in a February 24, 1984 package. This list, with minor changes, contains the sites to be sampled exclusive of tier 5 sites. Tier 5 sites were to be selected by June 1, 1984 by the regions with approval by OWRS.

This Project Plan serves as the Quality Assurance Project Plan for the National Dioxin Study and provides an overview of the entire study. It also serves as a integrated description of requirements in the field (Ref. No. 9) and laboratory (Ref. Nos. 7 and 8). The document provides specific QA guidance to the regions.

Two types of regional plans are required; each region will provide an overall work plan and a series of site-specific plans.

Contents of the regional work plan are to include: (1) a brief organizational section; (2) a tentative schedule for sampling at tiers 3, 5, 6, and 7; (3) a plan for using all the extramural funds; (4) arrangements (e.g., ESD, FIT, contractor, states, etc.) for sampling within each tier; and (5) a tier 7 sampling plan. Regional work plans were due to Headquarters on June 1, 1984.

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

MAR 18 1987

OFFICE OF WATER

Response to Item 3 as it pertains to paper mill study also enclosed.

Ms. Carol Van Strum
Route 2, Box 190
Tidewater, Oregon 97390

Re: Freedom of Information Act Request RIN 1102-87

Dear Ms. Van Strum:

This letter is in partial response to your Freedom of Information Act (FOIA) request of February 27, 1987, received by the Agency on March 4. It addresses Item 2 of your request. Items 1 and 3 are being answered by separate response.

We are treating Item 2 of your letter as a new request. Based on the information supplied with this request, we are granting your request for a waiver of fees.

Item 2 of FOIA Request

We are providing the records you requested relating to the joint EPA/paper industry screening study of dioxin in pulp and paper mills as follows. Please note that since your request includes two items marked "g" and two marked "h," we have changed the second set of "g" and "h" to "j" and "k," respectively.

a. We are sending you, under separate cover, all draft protocols and quality assurance project plans which have been prepared to date (as well as a listing of them). These draft documents are subject to revision to reflect, among other things, the final analytical methods chosen. In addition, we are providing the individual site sampling plans for the five mills participating in the study. No other records are responsive to Item 2a.

Included

b. and c. EPA possesses raw data sheets and draft data reports on samples which were analyzed as part of the process of developing analytical methods to meet the objectives of the study. That is, when the study was initiated, we recognized that there

To be sent by 4/1/87

EXHIBIT A

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

OFFICE OF
WATER

MAR 18 1987

Ms. Carol Van Strum
Route 2, Box 190
Tidewater, Oregon 97390

Re: Freedom of Information Act
Request RIN 1102-87

Dear Ms. Van Strum:

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a. We are sending you, under separate cover, all draft protocols and quality assurance project plans which have been prepared to date (as well as a listing of them). These draft documents are subject to revision to reflect, among other things, the final analytical methods chosen. In addition, we are providing the individual site sampling plans for the five mills participating in the study. No other records are responsive to Item 2a.

b. and c. EPA possesses raw data sheets and draft data reports on samples which were analyzed as part of the process of developing analytical methods to meet the objectives of the study. That is, when the study was initiated, we recognized that there

were likely to be some problems in performing reliable laboratory analyses including 1) achieving the very low detection levels needed to identify potential sources of dioxin within the mills (the study's target detection level for wastewaters is 10 parts per quadrillion, or approximately 1,000,000 times lower than is generally achieved on analyses of organic compounds in wastewaters); 2) being able to separate the dioxins and furans from the large number of interfering compounds found in pulp and paper mill wastes; 3) being able to distinguish among the many dioxin and furan isomers. The problems were interrelated and often compounded each other, as we discovered during some preliminary runs where we had levels of detection that were much higher than acceptable, ie., we wanted to be able to detect at much lower levels of occurrence. Therefore, the initial focus of the analytical phase of the study has been to perform a number of experiments to attempt to develop reliable analytical methods. These experiments involved using different sample preparation and clean-up procedures to remove interfering compounds and modifying the analytical instruments to improve their ability to distinguish among the different dioxin and furan isomers.

This experimentation process involved performing multiple analyses of individual samples. Accordingly, the data reports provide different results for the same samples, including at least one case where both "detected" and "nondetected" results were reported for a sample.

Therefore, the raw data and draft data reports which we have thus far generated only provide information about these "test runs," rather than providing information for use in the study itself. In short, the data you are being provided is essentially that collected during test method development and validation. Most of it was generated using test methods that were found to be inadequate and will not be used. EPA believes most strongly that other use of these data (such as to characterize the samples) is incorrect. EPA does not know if these test results show what is actually in the samples. The study data do not yet exist, except to the extent that we eventually may be able to use one or two data points from the test runs. While we are not certain whether you are interested in the test run data, we are sending them to you in case you are. We are in the process of collecting the raw data sheets and draft data reports for this response. We expect that they will be ready to be sent to you within the next two weeks.

At the time the samples were collected, certain physical characteristics were measured and noted. These included such factors as pH and temperature. We do not plan to send you this information since we understood your request to seek data related to dioxins and furans. However, should you wish to have this information as well, please let us know.

d. We have had a number of verbal discussions about

possible sources of dioxins in pulp and paper mills, but EPA has not prepared nor received any written record concerning the generation of dioxin in these mills. Much of our discussion has focused on the chlorine bleaching process, which is reflected by the emphasis on bleach plant wastewaters in the site sampling plans (see records responsive to Item 2a) and in some of the correspondence responsive to Item 2h. EPA expects that the results of the study will identify where in the process dioxin is being generated or introduced. At this time, no records exist responsive to Item 2d.

e. In response to this item, we are sending, under separate cover, all records, including laboratory reports, data summaries and miscellaneous documents, which contain information on levels of dioxins in pulp and paper mill wastewater treatment sludges. A list of these records also is being sent. In addition, some of the correspondence provided in response to Item 2h also may be considered to be responsive to 2e.

f. and g. We have verbally speculated about possible alternatives for reducing or eliminating dioxin discharges from pulp and paper mills, but there have been no written records on this. EPA is awaiting the results of the study to identify the sources of dioxins before undertaking investigations of control alternatives. Therefore, there are no records responsive to Items 2f and g.

h. All records responsive to this item are being sent to you under separate cover. The relevant correspondence begins with EPA's March 5, 1986 letter sent under authority of Section 308 of the Clean Water Act. The industry response to this letter precipitated discussions resulting in the joint study.

i. No decision documents have been prepared concerning the conduct of further studies of dioxin in pulp and paper mills. Based on the findings of dioxin in sludges (see response to Item 2e), EPA representatives met in February of 1986 and decided, as a first step, to conduct a detailed study of the mill described in the Section 308 letter mentioned above. While there are no documents responsive to this item (because there are no documents reflecting "decisions") some of the records provided in response to Items 2e and 2h discuss alternative courses of action.

j. No documents exist which are responsive to this item.

k. No documents exist which are responsive to this item.

We are providing lists of documents identifying all records responsive to Items 2a through h of your request. Please note that while we believe we have accounted for all responsive records, we are checking with our regional offices to make

certain that no records have been missed. If any additional records are located, we will be notified within the next two weeks and will inform you promptly of whether those records will be released or withheld.

If you have any questions concerning these records, please contact Alec McBride at (202)382-7046.

Sincerely,

William A. Whittington

William A. Whittington, Director
Office of Water Regulations
and Standards

UNITED ST/
ENVIRONMENTAL PROT
REGION V
EASTERN DISTRICT OFFICE
25089 CENTER RIDGE ROAD
WESTLAKE, OHIO 44145

2C-2

October 3, 1986

Mr. Russell O. Blosser
National Council of the Paper Industry
for Air and Stream Improvement, Inc.
260 Madison Avenue
New York, NY 10016

Re: USEPA/Paper Industry Cooperative
Dioxin Screening Study
March 1986 Preliminary Samples

Dear Mr. Blosser:

Today I received Dr. Tiernan's analytical method development report for the preliminary samples collected in March 1986. The full report has been sent under separate cover to Frank Thomas and Larry LaFleur for quality assurance review. The purposes of this letter are to advise you of the results for the preliminary samples contained in the analytical methods report (see attached handwritten data tables), and to request that NCASI secure from the paper company the analytical methods report and results for in-plant preliminary samples. Copies of that report should be provided to Frank Thomas, Larry LaFleur, and me as soon as possible.

The attached data, along with the results of external quality control samples for Episode 3018 (Dow Chemical analyses) suggest that the tetrachlorinated dioxins and furans are the principal species present in these samples. If this is confirmed by data from another mill, I believe we should reevaluate our analytical strategy and direct more resources at Dioxin 1 analyses and less at the more costly Dioxin 2 analyses.

CVS Note:
Boise Cas. Int'l Falls
- 3018
Crown Z Wawa O
- 3021
Champ. Int'l Lufkin
- Tx 3020
Mead Chillicothe OH
- 3019
3017 - @ Int' Paper Jay Maine

Per my conversation with Jim McKeown, I suggest we conduct a conference call during the afternoon of Wednesday, October 8, 1986, to discuss this further.

Sincerely yours,

Gary A. Amendola
Technical Project Manager

Enclosures

cc: Alec McBride
James McKeown
Ray Whittemore

Amendola
10-3-86

Preliminary Sampling March 1986
Results in Parts Per Trillion

Sample	Station 5 Bleach Plant, Tank Farm	Station 2 Paper Machines, Beater Rm	Station 6 Kraft, Recovery	Final Effluent	
USEPA Sample No.	86EB06507	508	506	510	
WSU Sample No.	BCP6-15,16 WW-5	BCP6-27 WW-2	BCP6-7,8 WW-6	BCP6-23,24	
2378-TCDD	1.08	ND (0.093)	ND (0.019)	0.251	(47.3% R
TCDDs	1.08	ND (0.007)	ND (0.015)	0.320	
PeCDDs			ND (0.008)	ND (0.019)	
HxCDDs			ND (0.015)	ND (0.021)	
HpCDDs			ND (0.019)	ND (0.024)	
OCDD			0.043 *	0.154 *	
2378-TCDF	3.91	0.450	ND (0.016)	1.03	(48.7%
TCDFs	6.64	0.803	ND (0.016)	1.52	
PeCDFs			ND (0.007)	ND (0.113)	
HxCDFs			ND (0.012)	ND (0.132)	
HpCDFs			ND (0.018)	ND (0.034)	
OCDF			ND (0.017)	ND (0.049)	

* LAB BLANK CONTAMINATION 0.0353

7

Amendola
10-3-86

PRELIMINARY SAMPLING MARCH 1986
RESULTS IN PARTS PER TRILLION

SAMPLE	WWTP COMPOSITE SLUDGE	WWTP COMPOSITE SLUDGE
USEPA SAMPLE No.	86EB06509	309
WSU SAMPLE No.	BCP6-14 TABLE 39	BCP6-14 TABLE 52
2378-TCDD	70.5	59.4
$TCDD_s$	71.9	59.4
$PeCDD_s$	ND (9.07)	ND (7.0)
H_xCDD_s	ND (13.8)	ND (6.0)
H_pCDD_s	ND (9.17)	ND (6.6)
OCDD	33.6 *	61.2
2378-TCDF	276	278
$TCDF_s$	384	418
$PeCDF_s$	ND (22.5)	ND (34.0)
H_xCDF_s	ND (22.0)	ND (24.0)
H_pCDF_s	ND (4.54)	ND (6.9)
OCDF	ND (41.9)	ND (34.0)

* LAB BLANK CONTAMINATION 0.0353

AMENDOLA
10-3-86

PRELIMINARY SAMPLING MARCH 1986

RESULTS IN PARTS PER TRILLION

SAMPLE	YELLOW DYE	CLAY	BLUE DYE	ALUM	SLIMICIDE
USEPA SAMPLE No.	86EB06515	S14	S11	S13	S12
WSU SAMPLE No.	BCP6-9 SPMD-2	BCP6-10 SPMC	BCP6-11 SPMD-1	BCP6-13 SPMA	BCP6-21 SPMS
2378-TCDD	ND (0.448)	ND (0.518)	3.36	ND (0.681)	ND (0.707)
TCDDs	ND (0.433)	ND (0.430)	52.8	ND (0.494)	ND (0.623)
PeCDDs					
HxCDDs					
HpCDDs					
OCDD					
2378-TCDF	ND (0.767)	ND (0.553)	ND (0.498)	ND (0.443)	ND (0.682)
TCDFs	ND (0.575)	ND (0.499)	ND (0.556)	ND (0.440)	ND (0.688)
PeCDFs					
HxCDFs					
HpCDFs					
OCDF					

AMENDOLA
10-3-86

PRELIMINARY SAMPLING RESULTS IN | MARCH 1986 PARTS PER TRILLION

SAMPLE	BLEACHED SOFTWOOD PULP
USEPA SAMPLE No.	SO5-B
WSU SAMPLE No.	BCP6-5B SPB-4 TABLE 52
2378-TCDD	8.4
$TCDD_s$	8.4
$PeCDD_s$	ND (1.0)
$HxCDD_s$	ND (0.7)
$HpCDD_s$	ND (0.9)
OCDD	2.1
2378-TCDF	62.3
$TCDF_s$	89.6
$PeCDF_s$	ND (1.3)
$HxCDF_s$	ND (1.4)
$HpCDF_s$	ND (0.9)
OCDF	ND (1.0)

2C-1

UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY
REGION V
EASTERN DISTRICT OFFICE
25089 CENTER RIDGE ROAD
WESTLAKE, OHIO 44145

September 16, 1986

Mr. Russell O. Blosser
National Council of the Paper Industry
for Air and Stream Improvement, Inc.
260 Madison Avenue
New York, NY 10016

Re: USEPA/Paper Industry Cooperative
Dioxin Screening Study
Episode 3018

Dear Mr. Blosser:

Per our September 15, 1986, telephone conversation, please find enclosed the results of external quality control analyses for four samples conducted by the Dow Chemical Company at USEPA's request. Also attached are the associated wastewater flow data for samples DE020915 and DE020922. Note that sample DE020923 is the NCASI quality control sludge. The laboratory analytical package for these samples will be sent directly to Larry LaFleur and Frank Thomas for quality assurance review as soon as I receive it from Dow Chemical. In the interim, these data should be treated as preliminary results subject to USEPA/NCASI quality assurance review.

I suggest that we conduct a conference call after you evaluate these data for the purpose of reviewing the analytical priorities established for Episode 3018 and subsequent sampling programs.

I look forward to hearing from you soon.

Sincerely yours,

Gary A. Amendola
USEPA Technical Project Manager

Enclosures

cc: Alec McBride, USEPA (WH-553)
Frank Thomas, USEPA, CRL
James J. McKeown, NCASI
Larry LaFleur, NCASI

DOW CHEMICAL U.S.A.

MICHIGAN DIVISION
MIDLAND, MICHIGAN 48640

September 4, 1986

Mr. Gary A. Amendola
U.S. EPA - Region V
Eastern District Office
25089 Center Ridge Road
Westlake, OH 44145

Dear Gary:

Enclosed are the final results of the Paper Industry samples from our Analytical Laboratory.

If you have any questions about these results, please don't hesitate to call me.

Sincerely,

JMR10/pe

J. M. Rio, Manager
Environmental Services
628 Building
636-2646

/pe

Enclosure

Quality Performance
Means More At Dow

AL 86-50583
02SEP86

Notebook REF: AL-3050 p.142
AL-3061 p.113

EPA PAPER INDUSTRY STUDY : DOW CHEMICAL RESULTS

DIOXINS [c]	PARTS PER QUADRILLION: Based on total sample weight (liquid + solids) DE 020915: WATER [a] 3050-150-1 CDD #1 1793.7g	DE 020922: WATER [a] 3050-150-2 CDD #2 1631.5g	PARTS PER TRILLION: Based on calculated sample dry weight DE 020920: SOLID [b] 3050-150-3 CDD #3 5.05g DRY	DE 020923: SOLID [b] 3050-150-4 CDD #4 8.90g DRY	ISOMER SPECIFICITY NOTES
2378-TCDD	150	73	17	240	Isomer Specific
^{13}C-2378-TCDD % Recovery	72%	66%	65%	87%	
12378-PCDD	6 (6)[d]	nd (7)	nd (1)	25	Unknown Specificity
^{13}C-12378-PCDD % Recovery	70%	86%	70%	100%	
123789-HCDD	nd (20)	nd (20)	nd (7)	6 (3)	Isomer Specific
123678-HCDD	nd (15)	nd (15)	nd (7)	9 (5)	Isomer Specific
123478-HCDD	nd (15)	nd (15)	nd (7)		Isomer Specific
^{13}C-123678-HCDD % Recovery	79%	82%	76%	64%	
1234678-H$_7$CDD	45 (10)	30 (15)	nd (6)	150	Isomer Specific
^{13}C-1234678-H$_7$CDD % Recovery	86%	70%	58%	85%	
OCDD	220 (40)	220 (30)	59 (9)	1400	
^{13}C-OCDD % Recovery	78%	89%	75%	84%	
Weight % H_2O Content →	(weight loss on drying at 105°C for ~21 hrs)		66.4% H_2O	10.9% H_2O	

FURANS [c,e]	DE 020915: WATER [a] 3108-8-1 CDF #1 1793.7g	DE 020922: WATER [a] 3108-8-2 CDF #2 1631.5g	DE 020920: SOLID [b] 3108-8-3 CDF #3 5.05g DRY	DE 020923: SOLID [b] 3108-8-4 CDF #4 8.90g DRY	ISOMER SPECIFICITY NOTES
2378-TCDF	2 500	1 000	300	2 300	Unknown Specificity
^{13}C-2378-TCDF % Recovery	82%	62%	68%	88%	
23478-PCDF	23 (3)	16 (3)	3 (1)	53	Unknown Specificity
12378-PCDF	27 (3)	16 (2)	3 (1)	140	Unknown Specificity
^{13}C-12378-PCDF % Recovery	81%	79%	83%	87%	
234678-HCDF	nd (5)	nd (5)	2 (2)	3 (1)	Unknown Specificity
123789-HCDF	nd (7)	nd (5)	nd (2)	<4 [f]	Unknown Specificity
123678-HCDF	9 (2)	5 (3)	1 (1)	20	Unknown Specificity
123478-HCDF					Unknown Specificity
^{13}C-123478-HCDF % Recovery	85%	103%	89%	89%	
1234789-H$_7$CDF	nd (10)	nd (10)	nd (3)	5 (2)	Isomer Specific
1234678-H$_7$CDF	10 (5)	7 (7)	2 (2)	11	Isomer Specific
^{13}C-1234678-HCDF % Recovery	91%	62%	79%	79%	
OCDF (absolute observed)	30 (15)	20 (10)	5 (5)	45	

[a] Filtered thru Whatman GF/C (dp = 1.2 μm): SOLID fraction → benzene Soxhlet, FILTRATE → 10% benzene in hexane liquid/liquid; extracts combined.
[b] Wet solid dispersed on Whatman GF/C filters → benzene Soxhlet. Concentrations reported on DRY WEIGHT basis.
[c] Native concentrations corrected for internal standard recovery as noted for each congener group; except OCDF → assumed 100% recovery.
[d] Values in parentheses are Limit of Detection = 2.5× peak to valley noise in adjacent region of SIM mass chromatogram; nd = not detected.
[e] Appropriate ions monitored to demonstrate no interference by potential presence of chlorinated diphenyl ethers.
[f] Maximum possible concentration; presence of large "non-CDF" interference prevents accurate quantitation.

TABLE 2

U.S. ENVIRONMENTAL PROTECTION AGENCY/PAPER MILL INDUSTRY
COOPERATIVE DIOXIN SCREENING STUDY

Episode: 3018

Sample Date: 6/24-25/86

Field Data Summary

Sample Number: DE020

	801 Treated River Water	806 Combined Pulping & Recaust	807 Combined Recovery Plant	811 Combined Paper Machine	915 Combined Bleach Plant	921 Combined Untreated Wastewater	922 Final Wastewater Effluent	821 Landfill Leachate
Sample Type	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	24 EVC	G
Date	6/24-25/86	6/24-25/86	6/24-25/86	6/24-25/86	6/24-25/86	6/24-25/86	6/24-25/86	6/24/86
Time	1905/1600	1706/1525	1945/1700	1940/1617	1720/1545	2005/1550	1955/1730	1440
Field Parameter								
Flow (MGD)	--	5.5	0.17	4.2	7.6	--	23.3	0.18
pH Range (s.u.)	5.34-7.09	10.34-11.06	9.00-10.84	3.66-9.06	2.55-2.79	6.21-7.46	6.01-6.83	--
Conductivity (umhos)	*		*				*	
Range		1300-1860		380-700	1700-2600	1000-1550		--
Average		1586		470	2234	1275		--
Temperature (°C)								
Range	17.9-20.1	34.8-39.7	17.8-20.8	26.0-30.4	28.2-33.9	25.8-32.3	28.1-33.2	--
Average	18.7	36.7	18.9	27.6	31.3	29.6	30.4	--

* Meter malfunction.

Sample Type: 24 EVC - 24-Hour Equal Volume Composite
G - Grab

2C-3

ncasi report

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT, INC., 260 MADISON AVENUE, NEW YORK, N.Y. 10016

RESULTS OF NCASI ANALYSIS OF CROWN ZELLERBACH, WAUNA SAMPLES FOR SELECTED CHLORINATED PHENOLIC COMPOUNDS

Lawrence E. LaFleur
Ken Ramage

November 1986

WEST COAST REGIONAL CENTER
P.O. BOX 458
CORVALLIS, OR 97339
(503) 754-2015

ncasi

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT, INC.

January 9, 1987

MEMO TO: Russell Blosser and Gary Amendola

FROM: Larry E. LaFleur

SUBJECT: Chlorophenol Analysis Reports For EPA/Paper Industry Cooperative Dioxin Screening Study Episodes 3010 (Boise Cascade, International Falls) and 3021 (Crown Zellerbach, Wauna).

Enclosed are reports summarizing our chlorophenol analysis results for the first two co-operative study sampling episodes. Should you have questions about the reports or the data please don't hesitate to contact me.

All the tables were prepared from Symphony spreadsheet files and could be provided on disk if that format would be more useful to your purposes.

TABLE OF CONTENTS

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II	ANALYTICAL METHODS	1
III	QUALITY CONTROL/QUALITY ASSURANCE	1
IV	RESULTS	2
V	LITERATURE REFERENCES	2

RESULTS OF NCASI ANALYSIS OF CROWN ZELLERBACH, WAUNA SAMPLES FOR SELECTED CHLORINATED PHENOLIC COMPOUNDS

I INTRODUCTION

The Crown Zellerbach, Wauna, Oregon, mill was the second mill sampled in the USEPA/Industry Cooperative Dioxin Screening Study. The sampling took place from September 8 to 9, 1986. Samples of selected wastewater streams and effluents which were designated for chlorinated phenolics analysis were split and sent to the NCASI West Coast Regional Center. This splitting provided external quality assurance on the contract laboratory and, since no analytical protocol had yet been developed by the Wright State University laboratory for the analysis of chlorinated phenolic compounds, provided added assurance that at least some data would be available. The following summarizes the results of the analysis of those split samples.

II ANALYTICAL METHODS

All samples were analyzed by NCASI Method CP-86.01, Chlorinated Phenolics in Water by In Situ Acetylation/GC/MS Determination, as described in NCASI Technical Bulletin No. 498 (1) except two stable isotope internal standards were used to improve the quantitation. The $^{2}H_{3}$-2,4-dichlorophenol and $^{13}C_{6}$-pentachlorophenol internal standards were spiked into the sample prior to acetylation and extraction. The quantitation technique described in EPA Method 1625 (2) was used except a three point calibration procedure was used. The recoveries of the internal standard were calculated based on calibration using the 3,4,5-trichlorophenol internal standard normally used for quantitation. The stable isotope internal standard recoveries are helpful in assuring meaningful spike levels were used (that is, the contribution of the native ion to the internal standard quantitation ion was minimal), that there were no major interferences with the stable isotope internal standard and where the analytes were not detected, as an in sample demonstration of method recovery.

III QUALITY CONTROL/QUALITY ASSURANCE

A method blank was run concurrent with the acetylation and analysis of the samples. None of the analytes were detectable in the blank.

Sample 86-37-4644 (untreated wastewater) was selected for quality assurance duplicate and native spike since it represented the combined bleach plant sewers and was amongst the most difficult matrices. The duplicate and native spike recovery data is summarized in Table 1. The relative percent differences were all less than 20 percent except for two of the chlorinated vanillins. These relative differences were higher as would be expected for

results near the detection limits of the method. Although two native spikes were conducted, the spike levels were at slightly different levels therefore additional information on the precision of non-detected analytes is not available. The recoveries were, however quite satisfactory. Future sample sets will include true spike duplicates to provide information on the precision of the method for analytes which are not routinely detected.

IV RESULTS

The results of the analysis of the samples are summarized in Table 2. Although detection limits for individual analytes are not specifically calculated, we estimated them to be in the 1 to 3 µg/L range. Although the relatively low recovery of $^{2}H_{3}$-2,4-dichlorophenol in samples 86-37-4601 and 86-37-4617 suggests some volatilization losses, they still fall within the range that would be acceptable in EPA Method 1625 and the remaining recoveries seemed satisfactory.

V LITERATURE REFERENCES

(1) NCASI Technical Bulletin No. 498, NCASI Methods For The Analysis of Chlorinated Phenolics in Pulp Industry Wastewaters (July 1986).

(2) EPA Method 1625, Revision B., Semivolatile Organic Compounds by Isotopic Dilution GC/MS, Federal Register, Vol. 49 No. 209.

TABLE 1 SUMMARY OF DUPLICATE AND RECOVERY DATA FOR SAMPLE 86-37-4644

Analyte	Duplicate Data			Recovery Data			
	Rep #1	Rep #2	Relative Percent Difference	µg/L Spiked	Percent Recovery	µg/L Spiked	Percent Recovery
2-Chlorophenol	ND	ND	NA	48.9	99	39.1	97
2,6-Dichlorophenol	ND	ND	NA	43.9	107	35.1	95
2,4-Dichlorophenol	10.7	8.8	19.0	34.2	110	27.4	82
3,4-Dichlorophenol	ND	ND	NA	39.3	109	31.4	98
2,3-Dichlorophenol	ND	ND	NA	43.7	112	35.0	105
2,4,5-Trichlorophenol	ND	ND	NA	39.8	119	31.8	88
Pentachlorophenol	ND	ND	NA	40.3	126	32.2	98
4,5-Dichloroguaiacol	4.4	5.2	17.0	34.7	117	27.7	94
3,4,5-Trichloroguaiacol	8.7	9.0	3.0	23.8	100	19.0	97
4,5,6-Trichloroguaiacol	3.2	3.3	3.0	40.6	112	32.5	111
Tetrachloroguaiacol	6.2	6.3	2.0	25.9	107	20.7	127
5-Chlorovanillin	1.9	2.5	27.0	28.1	107	22.5	130
6-Chlorovanillin	6.5	6.4	2.0	39.0	121	31.2	112
5,6-Dichlorovanillin	2.1	1.2	53.0	33.5	113	26.8	131
Isotope Percent Recovery							
$^{2}H_{3}$-2,4-Dichlorophenol	75	91			94		96
$^{13}C_{6}$-Pentachlorophenol	110	108			81		102

ND = Not Detected
NA = Not Applicable

TABLE 2 SUMMARY OF RESULTS OF ANALYSIS OF CROWN ZELLERBACH, WAUNA

Analyte	Concentration Detected (µg/L)								
	86-37-4601	86-37-4613	86-37-4614	86-37-4615	86-37-4616	86-37-4617	86-37-4644	86-37-4645	86-37-4646
2-Chlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,6-Dichlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4-Dichlorophenol	ND	9.7	ND	43.6	3.7	ND	9.8	0.2	ND
3,4-Dichlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,5-Dichlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,3-Dichlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4,5-Trichlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pentachlorophenol	ND	0.7	ND	6.1	4.0	1.8	ND	ND	ND
4,5-Dichloroguaiacol	ND	4.8	1.4	196	15.9	5.6	4.8	ND	ND
3,4,5-Trichloroguaiacol	ND	14.3	6.6	351	31.5	11.3	8.9	2.3	ND
4,5,6-Trichloroguaiacol	ND	7.3	0.9	146	68.5	11.8	3.3	1.7	ND
Tetrachloroguaiacol	ND	14.1	4.8	170	81.4	21.0	6.3	2.8	ND
5-Chlorovanillin	ND	ND	ND	24.4	15.0	4.6	2.2	1.9	ND
6-Chlorovanillin	ND	5.6	ND	163	19.6	8.9	6.5	4.2	ND
5,6-Dichlorovanillin	ND	6.1	ND	97.0	64.8	14.7	1.7	3.2	ND
Isotope Percent Recovery									
$^{2}H_{3}$-2,4-Dichlorophenol	46	77	54	90	95	39	83	99	83
$^{13}C_{6}$-Pentachlorophenol	94	137	183	131	103	89	109	101	111

ND = Not Detected

23-16

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

JUL 31 1986

OFFICE OF
WATER

MEMORANDUM

SUBJECT: Bioaccumulation Study Project Plan and Related Materials

FROM: Alec McBride, Chief
Water Quality Analysis Branch (WH-553)

TO: Regional Study Coordinators

Attached are the final project plan for the bioaccumulation study (Attachment 1) and a memorandum from Bill Whittington, OWRS Director, to the ESD and Water Division Directors (Attachment 2), which summarizes the background, objectives, and management framework for the study.

The project plan incorporates the major issues resolved at the Dallas meeting. The list of analytes has undergone further revisions which included dropping chemicals that: 1) have BCF values less than 300, since the projected human exposure from consuming fish is less than that from drinking water, 2) are quickly metabolized in fish or hydrolyzed, and 3) have analytical difficulties, such as lacking analytical standards. The list is still somewhat flexible as compounds may be removed due to operational analytical difficulties or added if they are of concern and standards and methods are available or can be developed.

Most of the sites each region recommended are included in the study. Fish sampling sites associated with paper mills using the bleach kraft process, however, are not included as part of this study. Instead, by August 15 we will review the list of 145 mills identified by NCASI as those which use the bleach kraft process (Attachment 3) and identify which had fish sampled nearby during the dioxin study. For the remaining mills on the list which are active dischargers, we would like you to arrange to collect and analyze downstream fish samples through the Wright State contract managed by ORD-Duluth. Funding adjustments will be made in FY87 to ensure that these analyses can be completed.

As discussed previously, we have deposited the remaining FY86 dioxin study funds in the Wright State contract. Each region

(with a couple of previously negotiated exceptions) has approximately $15,000 available in that contract for analytical support, and those funds need to be spent by May 1, 1987. In order to use your funds, first contact Dr. Tom Tiernan (513-873-2202) at Wright State to discuss your needs and the estimated hours and dollars for each task. After consulting with Tom, fill out a work assignment form (Attachment 4) and send one copy to Fred Freeman, Project Officer, ORD-Duluth and one copy to us. Fred will see to it that the assignment goes through the proper contract channels. A fish sample analysis for 2,3,7,8-TCDD only should run about $600.

The Sample Control Center (SCC) will track the sampling and analytical effort for both the fish samples from below paper mills and for the bioaccumulation study. Prior to sampling, please contact Jim King with the SCC (FTS 557-5040) to obtain identification information and shipment records for each site. We will be working with ORD-Duluth to set up a data management system for accessing the analytical results. We hope to have this system working by November, which is the earliest we expect data to be available.

Please let me know if you have any questions regarding implementation of the study or its funding.

Attachments

cc: Doug Kuehl
Pete Redmon
Martin Brossman
Dave Terpening
Bob Kleopfer
Fred Leutner
Gary Amendola

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

JUL 28 1986

MEMORANDUM

SUBJECT: Description of the Bioaccumulation Study

TO: Regional Water Division Directors
Regional Environmental Services Division Directors

The Monitoring and Data Support Division (MDSD) will soon initiate sampling for a two-year study designed to investigate the bioaccumulation of selected toxic pollutants in fish. This bioaccumulation study is, to a large extent, an outgrowth of EPA's National Dioxin Study, which investigated the extent of 2,3,7,8-TCDD contamination in soil, fish, and air. Some of the samples collected during the dioxin study will be reanalyzed for this study. The focus of the study is on pollutants which are potential human health threats primarily through fish contamination, as opposed to pollutants which are more likely to affect humans through other exposure routes such as drinking water.

The impetus for the bioaccumulation study was the increasing awareness that fish consumption may be a significant human exposure route for toxic pollutants and the concern that there may be a number of uninvestigated pollutants with properties similar to 2,3,7,8-TCDD which could bioaccumulate in fish. In addition, as part of its response to a petition from the Environmental Defense Fund (EDF) and the National Wildlife Federation (NWF), EPA committed to conducting an aquatic monitoring survey for other chlorinated dioxins and dibenzofurans to support regulatory decisions relating to a number of provisions under the Clean Water Act.

The major objectives of the study are: (1) to indicate the overall prevalence and concentrations of approximately 70 selected pollutants in fish from locations (a) statistically selected from ambient monitoring networks, (b) in relatively undisturbed background areas, and (c) in areas with high concentrations of industrial discharges and/or high bioaccumulation potential; (2) to determine the levels of a limited subset of these pollutants in fish in the immediate vicinity of specific potential sources; and (3) to evaluate potential effects on human health.

Potential candidate chemicals came from several sources including lists of priority pollutants, non-convential pollutant pesticides found in effluents from pesticide manufacturing

facilities, chemicals identified by the Carcinogen Assessment Group (CAG) or the International Agency for Research on Cancer (IARC) as known or potential cancer-causing agents, organic compounds identified in human adipose tissue, pollutants identified as non-biodegradable in industrial and POTW effluents, and various compounds recommended by regional and laboratory personnel.

A total of approximately 400 compounds were screened for bioaccumulation potential in fish. Compounds not expected to bioaccumulate to a significant extent were removed from the list. The remaining chemicals were screened for potential toxic effects in humans and for projected biochemical fate in fish and the aquatic environment. Compounds that are quickly hydorolyzed or metabolized were also removed from the list. Finally, a few pollutants were dropped from the list based on analytical difficulties (extensive methods development needed or lack of analytical standards). The target list of approximately 70 analytes (Attachment 1) is not completely final since compounds may be removed due to operational analytical difficulties or added if they are of particular concern and methods can be developed.

For most of the analytes, MDSD was able to estimate fish tissue concentrations of concern to human health. These levels were derived from data on chronic toxicity or carcinogencity using procedures normally applied to water quality criteria development. These estimates were done to ensure that the analytical detection limits for each analyte were low enough to detect levels of concern as well as to assist in evaluating the results.

The initial subset of pollutants for which targeted sampling will take place include chlorinated dioxins and furans and hexachlorobenzene. The targeted sites were selected jointly by MDSD and the regional coordinators, who are listed in Attachment 2. As results from the study becomes available, additional pollutants will likely be selected for targeted sampling.

The study will be conducted in much the same way as the dioxin study was conducted. Overall study design was done primarily by MDSD, while site selection was done by both MDSD and the regional coordinators. MDSD will provide funding to the Regions to ensure that the field work is done and will provide access to sampling contractors where necessary. In most cases, the regional coordinators will use state agencies to do the field work. MDSD will also provide funding to ORD to provide analytical support. All participants will provide input to the final report, which MDSD will compile. We hope that this process will be as successful as it was for the dioxin study.

I will be sure to keep you updated as the study progresses. Please feel free to call me or Alec McBride (FTS 382-7046) if you have any questions or comments on the study. We do have some flexibility in how we proceed, and I would appreciate any thoughts you might have on things we should be investigating.

Attachments

William S. Whittington

William A. Whittington, Director
Office of Water Regulations and
Standards (WH-551)

Attachment 2. Regional Bioaccumulation Study Coordinators

Region	
I	Bill Walsh, ESD
II	Rick Spear, ESD
III	John Ruggero, ESD
IV	Ron Raschke, ESD
V	Howard Zar, Water
VI	Dave Parrish, ESD
VII	Billy Fairless, ESD
VIII	Dean Gillam, ESD
IX	Kathleen Shimmin, Toxics
X	Lori Cohen, Air and Toxics

Attachment 1. List of Target Analytes

Biphenyl
Butachlor
Chlorbenzilate
Chlordane, cis
Chlordane, trans

Chlorinated Dioxins & Furans:
- 2378-TCDD
- 12378-PeDD
- 123678-HxDD
- 123789-HxDD
- 123478-HxDD
- 1234678-HpDD
- 2378-TCDF
- 12378-PeDF
- 23478-PeDF
- 123678-HxDF
- 123789-HxDF
- 123478-HxDF
- 234678-HxDF
- 1234678-HpDF
- 1234789-HpDF

Chlorpyrifos
p,p'-DDE
Dicofol (Kelthane)
Dieldrin
Diethylhexylphthalate (DEHP)
Diphenyldisulfide
Endrin
Heptachlor
Heptachlor epoxide
Hexachlorobenzene (HCB)
Hexachlorocyclohexanes (BHC) including Lindane

Isopropalin
Kepone
Mercury
Methoxychlor
Mirex
n-alkanes (C_{20-32})
Nitrofen
Nonachlor, cis
Nonachlor, trans
Octachlorostyrene
Oxychlordane
Pentachloroanisole
Pentachlorobenzene
Pentachloronitrobenzene (PCNB)
Pentachlorophenol
Perthane
Polychlorinated Biphenyls:
- Mono-Decachlorinated Biphenyls
- 3,4,3',4'-Tetrachlorobiphenyl
- 3,4,5,3',4'-Pentachlorobiphenyl
- 3,4,5,3',4',5'-Hexachlorobiphenyl
- Total PCBs

1,2,4,5-Tetrachlorobenzene
1,2,3,4-Tetrachlorobenzene
1,2,3,5-Tetrachlorobenzene
1,2,3-Trichlorobenzene
1,2,4-Trichlorobenzene
1,3,5-Trichlorobenzene
Trichloronate
Trifluralin
Triphenyl phosphate