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A REPORT PREPARED BY THE OFFICE OF RESEARCH AND DEVELOPMENT
FOR THE
SCIENCE ADVISORY BOARD

Prepared by:
U, S. Environmental Protection Agency "Dioxin Team"
Office of Research and Development

August, 1985

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EXECUTIVE SUMMARY

The Office of Research and Development (ORD) has prepared this report to be used as a briefing document for the EPA Science Advisory Board (SAB). As it describes the status of "dioxin"* research in EPA as of August 1985, it will serve as a support document at the SAB review of EPA's dioxin research, to be held at the Environmental Monitoring and Support Laboratory (EMSL), Las Vegas, Nevada. The SAB will transmit the findings of their review to the EPA Deputy Administrator.

Dioxin research at the Agency began in 1970, when 2,3,7,8-TCDD was found to be a contaminant of the commonly-used herbicide, 2,4,5-T. This research effort, however, was limited to developing methodology for detecting 2,3,7,8-TCDD in environmental samples. Additional impetus was generated in 1984, when the U. S. Congress enacted legislation specifically directed toward this class of chemicals. The 98th Congress appropriated specific resources for dioxin research in human toxicity, disposal methods, and sampling quality assurance. Congress allocated additional funds for a study of dioxins and other chlorophenols, which included both comprehensive monitoring of specific problem areas and a national screening study (called the Agency's "National Dioxin Study") to determine relative concentrations in other areas.

- The Agency's "Dioxin Strategy" is a direct response to both Congressional directives. It designates seven "tiers" to prioritize potential source categories from the highest to lowest expected exposures and risks. Tier 1, the highest of the seven source categories, included 2,3,5-TCP production and waste disposal sites; tier 2 included sites where 2,4,5-TCP was used as a precursor of another chemical; tier 3 covered those sites where 2,4,5-TCP and its derivatives were formulated into a pesticide product; tier 4 sites were combustion sources; tier 5 consisted of sites where 2,3,7,8-TCDD contaminated pesticides were being used; tier 6 had sites where 2,3,7,8-TCDD may have been inadvertently generated from other organic chemicals; and tier 7 covered control sites.

Early phases of the research were limited to the most toxic dioxin, 2,3,7,8-TCDD. The major emphasis of the research program was to develop technologies for detoxification of contaminated sites. It also sought the development of techniques for monitoring, sampling, and quality assurance in measuring this chemical, as well as an assessment of the health risks associated with dioxins, and an evaluation of their bioavailability. Through a workshop on "Bioavailability of Dioxins" in September 1984, the Agency obtained direct input from a broad range of scientific experts. EPA coordinated its efforts with those of other Federal agencies by means of a comprehensive information exchange, and by participation in the Agent Orange Work Group.

* The term "dioxin" as well as some of the other terms used in this report are defined at the end of Chapter I, the General Introduction,

By establishing an International Information Exchange under the North Atlantic Treaty Organization (NATO) committee on "Critical Challenges of Modern Society" (CCMS), the Agency has taken initiative to coordinate its research with other industrialized nations concerned with **dioxins**. The United States, the Federal Republic of Germany, and Italy are coordinators of this project.

There are four areas of EPA **dioxin** research: **technology assessment; monitoring;** environmental effects; and health assessment. Technology assessment research evaluates the available technologies for the **control**, and ultimate destruction or detoxification of dioxins. Monitoring research develops analytical methodologies and quality assurance procedures for identifying and quantifying dioxins within biotic and abiotic matrices. Environmental effects research considers the fate, mobility, and effects of "dioxins" in the environment, and determines the uptake and **bioavailability** in plants and living systems. Health assessment research develops both methodologies and the data base that is necessary for evaluating human health exposure and risks associated with dioxins and provides the Agency with the necessary documentation to perform exposure and risk analysis.

The research budget for dioxins was about \$2.4 million for **FY'84** and \$3.0 million for **FY'85**. Additional resources from "**Superfund**" supported a demonstration clean-up program using the EPA mobile incinerator.

Since the inception of this research program 22 months ago, the Agency has made significant progress in evaluating and refining techniques for clean-up of dioxins. This includes field work on **detoxification** of dioxin-**contaminated** soils using **U.V.** photolysis/Alkali Poly **Ethylene Glycolates** (APEG) reagents at a horse arena in Missouri; field testing of EPA mobile incineration system at the **Denney** Farm site near McDowell, Missouri; in-situ stablization testing using **portland** cement and lime-treated asphalt; and an evaluation of the utility of surface mines as repositories for dioxin-**contaminated** soils. Laboratory tests have shown that the white rot fungus, **Phanerochaete chrysosporium**, is capable of degrading **2,3,7,8-TCDD**, DDT, lindane, **PCBs**, and other recalcitrant **halogenated organics**; field testing will be the next step in the program.

At the onset of the program, there was a lack of analytical capability to routinely analyze a large number of samples containing dioxins. As part of the National Dioxin Study the Agency has developed a collaborative network of three of its laboratories (**ERL-Duluth; EMSL-RTP, NC; and ECL-Bay St. Louis, MS**). The collaborative effort of the three is referred to as "**TROIKA**", and its stated purpose is to analyze trace level dioxins in environmental media. TROIKA has **significantly** improved the **Agency's** analytical capability for measuring dioxins and has made a major contribution to the **state-of-the-art** of analysis of **2,3,7,8-TCDD**. The Agency has also made significant progress in parts per trillion (ppt) routine analysis of dioxins through a contract laboratory program. A round-robin survey of trace level analysis of dioxins in adipose tissues has been completed. Quality assurance has been provided to the "National Dioxin Study" and the mobile incinerator program. A monoclonal antibody to detect and measure dioxins is being developed.

Environmental effects studies have shown that dioxins are very tightly sorbed onto soils and that both organic contaminant content and actual organic matter are important factors in controlling their movement in soils. Uptake studies have shown that 2,3,7,8-TCDD, preferentially, in comparison to other isomers, bioaccumulates in fish. Bioavailability studies in laboratory samples of contaminated soils from Missouri and New Jersey have shown that bioavailability is complex and highly dependent on the nature of soil and the chemical constituents of the waste present. For example, the bioavailability of New Jersey soil compared to Missouri soil was negligible in laboratory test animals.

ORD has completed a document which describes methods to evaluate the health hazards associated with dioxins. Further, methods for evaluating exposure to humans from dioxin-contaminated soils have been developed. An ongoing pharmacokinetic study of 2,3,7,8-TCDD in rhesus monkeys will provide results on distribution, accumulation, depuration, and transfer of 2,3,7,8-TCDD in offspring. A battery of immunological tests to analyze the results of exposing female rhesus monkeys and their offspring to 2,3,7,8-TCDD is also being developed.

Future Agency research on dioxins will follow the extant Agency strategy, with modifications where these become desirable. More emphasis will be placed on studying other dioxin isomers. Technology assessment research will emphasize source characterization, development of lower-cost treatment technology, and the evaluation of combustion sources. Monitoring research will continue to develop reference standards, and to improve methods for analysis including short-term bioassays. Environmental research will continue to evaluate bioavailability in living systems in addition to pertinent toxicity information, as it becomes available. Health assessment research will be expanded to develop and improve methods for evaluating health effects and risks associated with dioxins.

CHAPTER I

GENERAL INTRODUCTION

This document has been prepared by the **Office** of Research and Development (**ORD**) of the U. S. Environmental Protection Agency as briefing material for the Environmental Protection Agency's Science Advisory Board (SAB) Review of "**Dioxin** Research" in EPA. This is one in a series of SAB reviews to evaluate **EPA's** major research **programs**, which submit the **Agency's** research to close scrutiny in order to make the **modifications** necessary to respond most effectively to its own objectives, and those of the scientific community.

The current **ORD** dioxin research is based on the objectives and needs identified in the **Agency's** "**Dioxin Strategy**", published in November of 1983. **This** strategy resulted from the Congressional mandate to study **dioxins**, and it assigned various responsibilities for dealing with the dioxin problem to **ORD** and to other Agency program **offices**. The earlier emphasis of the research program had been to provide solutions to short-term problems associated with the clean-up of dioxins.

The Agency has also coordinated this research with other Federal agencies through information exchange and through participation in the Interagency Agent Orange Work Group. The Agency has established an information exchange under the North Atlantic Treaty Organization (NATO) committee on "Critical Challenges of Modern Society" (**CCMS**) for the purpose of sharing dioxin information between the U.S. and the other participating countries. The United States of America, the Federal Republic of Germany and Italy are coordinating the project. NATO and selected non-NATO countries will be invited to participate in the exchange program. The orientation meeting was held in Brussels, Belgium in May of 1985. The first planning meeting is scheduled to be held in late September, 1985, in **Bayreuth**, Federal Republic of Germany.

This document includes sections on several facets of **EPA's** approach to the dioxin problem, including the **Agency's** historical involvement in dioxin research; regulatory needs and the EPA "**Dioxin Strategy**"; a regional perspective; and a description of ongoing dioxin research, including both major accomplishments and broad directions for future research.

Terminology used in this document includes:

1. "Dioxin" - Any and all of the congeners of **chloro-dioxins**. Although the word "dioxin" is not the true generic term for these congeners, for the purpose of this document, we will use it as such.

2. **Isomer** - one particular member of a homologous group. A specific **isomer** is denoted by unique chemical notation, for example, 2,3,7,8-tetrachlorodibenzo-**p**-dioxin refers to **2,3,7,8-TCDD**.

3. "Homologue" a group of isomers that have the same degree of halogenation. For example, the homologous class of TCDDs consists of those dibenzo-p-dioxins that have four chlorine atoms.

4. "Polyhalogenated dibenzo-p-dioxin" any member of a class of dibenzo-p-dioxins containing one to eight chlorine, bromine, or a combination of chlorine and bromine substituents. "Polychlorinated dibenzo-p-dioxin" refers to any member of a class of dibenzo-p-dioxins with one to eight chlorine substituents. "Polybrominated dibenzo-p-dioxin" refers to any member of a class of dibenzo-p-dioxins with one to eight bromine substituents.

5. "Polyhalogenated dibenzofuran" any member of a class of dibenzofurans with one to eight chlorine, bromine, or a combination of chlorine and bromine substituents. "Polychlorinated dibenzofuran" refers to any member of a class of dibenzofurans with one to eight chlorine substituents. "Polybrominated dibenzofuran" refers to any member of a class of dibenzofurans with one to eight bromine substituents.

6. 2,4,5-T refers to 2,4,5-Trichlorophenoxy acetic acid.

7. 2,4,5-TCP represents 2,4,5-Trichlorophenol.

CHAPTER II

THE DIOXIN **PROBLEM**: A HISTORICAL PERSPECTIVE

EPA has been involved with the **dioxin** issue since the **Agency's** inception (as indicated **below**, in the dioxin chronology). The Agency has contributed significantly to **developments** in both regulatory and scientific **ways**.

The clear regulatory need to determine the presence of 2,3,7,8-TCDD in the environment led the Agency in the **mid-1970's** to coordinate the efforts of scientists from both the public and private sectors to develop the general **method** which is still principally **used** today - gas **chromatography** coupled to mass **spectrometry**. The Agency is continuing to improve methods of analysis for **the entire** range of chlorinated **dibenzodioxins (CDDs)** and chlorinated **cibenzofurans (CDFs)**, in more **complex** matrices which are more rapid and reliable, and which can be implemented at lower cost.

Regulatory need led the Agency to develop a method for quantitative assessment of the risk associated with exposure to **2,3,7,8-TCDD**, which is being pursued as the Agency extends its assessment of **2,3,7,8-TCDD** into various environmental media, and develops methods for assessing risks associated with CDDs and CDFs other than **2,3,7,8-TCDD**.

The Agency must also address the pragmatic issue: "If you know the dioxins are present and that they are hazardous, what regulatory actions **need** to be taken?" EPA has **been** at the forefront of the national efforts to develop remedial measures for reclaiming areas which have been contaminated with **CDDs/CDFs**. The Agency continues to pursue a variety of approaches - from soil incineration to a technique which uses white rot fungus.

These and other fundamental contributions have **identified** the Agency as a primary reservoir **of** knowledge and experience in the CDD/CDF area. Consequently, EPA has been a contributing member to special groups convened to address **this problem**, including: the Veterans Administration Agent Orange Science Advisory **Committee** and the Cabinet **Council's** Agent Orange **Work** Group. In addition, the Agency has taken the initiative on the international scene, establishing, under NATO, a mechanism for the exchange of technical and regulatory information on CDD/CDF.

DIOXIN CHRONOLOGY

Early 1970s

- o Discovery of **the same teratogenic** effects in **2,4,5-T** as in **2,3,7,8-TCDD**.
- o **USDA** ban of 2,4,5-T for home and garden use.

- o Suspension of the military use of **Agent Orange** in **Vietnam**.
- o Creation of **"Dioxin"** Task Force (later called the **Chlorinated Dioxins Work Group**).

Mid-1970s

- o Initiation of a cancellation action against **2,4,5-T** by EPA.
- o Suspension of the regulatory action due to inability to detect **2,3,7,8-TCDD** in the environment; Agency examination of **2,4,5-T** continues under the **Rebuttable** Presumption Against Registration (**RPAR**) process.
- o Establishment of a joint **industry/government/academia** group, the Dioxin Implementation Program (later called the **"Dioxin" Monitoring Program**), to develop an analytical method for detecting **2,3,7,8-TCDD** at the parts per trillion **level** in environmental samples.
- o Discovery of contaminated sites in **Missouri**.
- o Explosion of a chemical reactor in **Seveso, Italy**.
- o Rising health concerns among Vietnam veterans.

Late 1970s

- o Development of sensitive analytical methods; **2,3,7,8-TCDD** is discovered in some environmental samples.
- o Announcement of an apparent association between forest spraying of **2,4,5-T** and spontaneous abortions.
- o Emergency suspension of **2,4,5-T** triggers legal proceedings which will last for years.
- o Discovery of an apparent association between exposure to **phenoxy** herbicides and the incidence of soft tissue sarcomas.
- o Investigation of Hooker Chemical sites **along** the **Niagara River** in New York leads to discovery of substantial amounts of **2,3,7,8-TCDD** in dump sites (**Hyde Park Landfill** and **Love Canal**).
- o Issuance of **immediately** effective rule under **TSCA** requiring notification of Agency prior to disposal of certain **2,3,7,8-TCDD-containing** waste.
- o Initiation of investigation of **CDD/CDF** emissions from municipal waste **combustors**.

- Discovery of emissions of **CDDs/CDFs** from **fires** associated with **PCB-containing electrical equipment**.
- Approval of high temperature incineration of **PCBs**: **TCDDs/TCDFs** are found to be associated with process.
- White House establishes an interagency group to study phenoxy herbicides and their **contaminants**; Addresses heightened concerns of veterans.

Early 1980s

- Expansion of interagency Agent Orange **Work Group (AOWG)** to include 15 member agencies; Major **epidemiology** studies are started.
- Presentation of "risk case" in **2,4,5-T** hearings, followed by suspension of hearings.
- Release of interim assessment of emissions from municipal waste **combustors (MWCs)**; No health concern raised at five facilities investigated.
- **CDD/CDF** emissions from **NASA/Hampton** Incinerator higher than previous **MWC sources**.
- Re-investigation of Missouri sites leads to discovery of more than forty **sites** in the State which are contaminated with **2,3,7,8-TCDD**.
- **Buy-out** of Times Beach.
- Elevation of "**dioxin** problem" to media stardom.
- Development of EPA "**Dioxin Strategy**".
- Promulgation of PCB Transformer Fires rule.

Mid 1980s

- Settlement of **2,4,5-T** case: Cancellation of all **uses**.
- Settlement of **veterans's** case against chemical **companies**.
- Initiation of the "**National Dioxin Study**". Includes collecting data on historically suspect areas, **combustion** sources, and "background" levels.
- Initial reports from various **epidemiological** studies: "worst case scenarios" not **confirmed**.
- Restrictions on production and use of **CDD/CDF-containing pentachlorophenol**.

- o Listing of certain CDD/CDF containing wastes under RCRA for special handling.
- o Action to investigate additional products which might contain dioxins (under TSCA and FIFRA).
- o Increased interest in dioxin problem on the international level; EPA promotes the establishment of a special committee under NATO to facilitate information exchange.

CHAPTER III

EPA "DIOXIN STRATEGY" AND REGULATORY APPROACH

EPA's "Dioxin Strategy" provides the focus for an integrated Agency program to assess and control environmental contamination and associated risks for CDDs and CDFs. This strategy was developed and implemented in late 1983 for the purpose of systematically investigating chemical production and waste sites suspected of being contaminated with CDDs/CDFs (primarily from 2,4,5-TCP), and to determine the extent of environmental contamination from these and other sources, principally combustion. In addition to integrating ongoing Agency activities related to CDDs/CDFs, the strategy is in direct response to a congressional appropriation which directed tiPA to conduct a "National Dioxin Study".

Although the original focus of the "Dioxin Strategy" was on the well-recognized toxic isomer 2,3,7,8-TCDD, it soon became apparent that a number of CDDs and CDFs were of environmental concern. AS a result, EPA research and regulatory activities now address CDD/CDF isomers in addition to 2,3,7,8-TCDD. Nonchlorine halogenated dibenzodioxins and dibenzofurans, which include the brominated analogs of CDDs/CDFs, are also of concern. The Agency is monitoring the available information to determine the need for action in this area.

In general, the purpose of the strategy was to focus and coordinate intra-agency activities related to assessing, cleaning up, and regulating CDDs/CDFs. EPA also recognized, and has depended on related CDD/CDF assessment and control activities through other Federal and State programs. In particular, the Veteran's Administration, Centers for Disease Control (CDC), the National Institutes for Occupational Safety and Health, and the Food and Drug Administration all have programs that are involved with evaluating the potential health and environmental risks from exposures to CDDs/CDFs, particularly 2,3,7,8-TCDD. EPA's integration of these activities is largely through the Agent Orange Work Group, and also through bi-monthly meetings with CDC.

SOURCE CATEGORIES FOR EXPOSURE AND RISK

To implement the strategy, a seven-tiered approach was designed so that the source categories with higher perceived potential for exposures and risks were given higher research priority. These tiers are defined and described below:

1. Tier 1 - Current (if any) and former sites of 2,4,5-TCP production, including sites where wastes were disposed. The number of tier 1 production sites is estimated to be about 20; the total number of sites to be investigated (production sites plus waste disposal sites) is not presently known.

2. Tier 2 - Sites (current and former) where 2,4,5-TCP was used as a precursor to make another chemical product (e.g., hexachlorophene, 2,4,5-T, and silvex) including sites where wastes were disposed. The number of tier 2 production sites is estimated to be about 30, exclusive of sites where wastes were disposed.
3. Tier 3 - Sites (current and former) where 2,4,5-TCP and its derivatives (e.g., silvex) were formulated into a pesticidal product. An example is a site where 2,4-D and 2,4,5-T were mixed to make Agent Orange. Tier 3 also includes sites where formulating wastes were disposed.
4. Tier 4 - Combustion sources, including: (1) incinerators of hazardous and municipal waste (including sewage sludge); (2) wire reclamation facilities; (3) internal combustion engines; (4) home heating units (e.g., wood burning stoves); (5) industrial, fossil-fuel fired boilers; and (6) inadvertent combustion sources such as PCB-transformer and capacitor fires. The number of sites potentially within this tier is estimated to be in the millions.
5. Tier 5 - Sites where 2,3,7,8-TCDD contaminated pesticides have been used or are being used on a commercial basis. These areas include certain rights-of-way; rice fields, including those in Arkansas and Louisiana; pastures and western rangeland; sugar cane fields in Florida and Louisiana; certain aquatic sites; and forests (e.g., Pacific Northwest). In addition, animals that have been grazed on treated land, and fish from treated waterbodies, both of which may contain 2,3,7,8-TCDD residues, will be studied.
6. Tier 6 - Sites where production of certain other organic chemicals or pesticides may have resulted in the formation of 2,3,7,8-TCDD, through improper quality control. The total number of production sites in this tier is probably less than 100.
7. Tier 7 - Control sites selected to evaluate the extent of dioxin contamination in areas where neither manufacturing nor extensive use of 2,3,7,8-TCDD contaminated chemicals has occurred. Information from these sites will be used to compare with sites where 2,3,7,8-TCDD is a known contaminant, and to establish "background" levels of 2,3,7,8-TCDD.

As data from the study tiers are assembled and analyzed, various regulatory options to prevent or control future CDD/CDF contamination are being evaluated and implemented. These options include further application of existing regulations, as well as the development of new regulations. Such actions as the RCRA waste stream listings, CWA Section 307(a)(2) listings, TSCA Section 6 rules, the Clean Air Act hazardous pollutant listings, and alternative management options (e.g., prohibiting certain dioxin-containing wastes from land disposal) are being implemented or evaluated.

A research program to support the overall strategy, common to all tiers, is an important component of the "Dioxin Strategy". The EPA/ORD dioxin research program has been developed both to provide CDD/CDF assessment methods, and to control technology evaluation and development.

The November 1983 "Dioxin Strategy" called for the following specific research support:

EPA/ORD would provide analytical services for all samples collected in tiers 3 to 7, with ORD selecting the appropriate sampling and analytical methods and defining the QA/QC specifications for 2,3,7,8-TCDD analysis in all tiers. ORD will support the Office of Solid Waste and Emergency Response in pilot testing the more promising disposal and destruction techniques for CDDs/CDFs. In addition, ORD will study the sorption/desorption of CDDs/CDFs within contaminated soils, particularly the effects of these phenomena, and their relation to the efficacy of treatment techniques. OKU, in conjunction with the Regions, would also conduct full field validation of incineration as a treatment option.

Using the best data at hand (carcinogenicity and reproductive effects), ORD would continue to coordinate hazard assessment techniques used by EPA in making site-specific risk assessments.

ORD in conjunction with the Chlorinated Dioxin working Group (CDWG) would also establish exposure scenarios to estimate exposure under the various conditions likely to be encountered in tiers 1 through 6.

In addition, ORD would develop a nomograph for converting from 2,3,7,8-TCDD levels of contamination in environmental media to estimates of upper risk limits for a variety of exposure scenarios. ORD would provide guidance to the Regions and States on use of exposure nomographs.

In other studies ORD would research the bioavailability and uptake mechanism of sorbed 2,3,7,8-TCDD. ORD would also investigate the transport and transformation processes (bioaccumulation and biomagnification) of 2,3,7,8-TCDD in fish, sediments, and plants for use in food chain models and establishment of acceptable levels.

Other research areas were judged to be of sufficient importance to the strategy that they should be **specifically** identified in any interagency **meetings** that are conducted to initiate health research. **These** included: (1) Understanding the **pharmacokinetic** mechanism of 2,3,7,8-TCDD induced toxicity, to determine differences between species in response to **2,3,7,8-TCDD**; (2) Understanding and developing the toxicological and analytical relationship between **2,3,7,8-TCDD** and "**2,3,7,8-TCDD** equivalents" in **complex** mixtures for more rapid and less expensive determinations of **2,3,7,8-TCDD** levels and effects; (3) Conducting **epidemiological** studies at contaminated sites to provide better information on risks for regulatory decisions. This work was to help establish the **cause/errect** relationship of **2,3,7,8-TCDD** to human **disease**.

As part of the development of an **inter-agency** program, ORD would work with the other Federal agencies to **develop** a research program which addresses the toxicology of the other dioxin **isomers** and the "**dioxin-like**" chemicals. Additional toxicity data are **needed**, especially for possible carcinogenic, reproductive, and teratogenic effects, and bioavailability of the halogenated dioxins and **dibenzofurans**.

Additionally ORD would work with CDC, the U.S. Fish and Wildlife Service, and other Federal agencies to develop analytical protocols to measure "dioxin-like" chemicals in biological tissues, waste emissions, and environmental media.

In the area of bioanalytical techniques, ORD would explore development and validation for estimating the toxicity of complex mixtures containing 2,3,7,8-TCDD and "dioxin-like" **compounds**. It was expected that such methods would reduce the need for the expensive and resource-intensive **isomer-specific** analysis of the mixtures associated with combustion and chemical processes.

In conjunction with the **CDWG**, ORD would develop and apply methods to predict the fate, persistence, and **bioaccumulation** potential of dioxins in the environment. These efforts would be made **in** conjunction with **development** of the sampling program discussed above. The results of these analysis would be combined with the source assessments and toxicity **studies** to provide interim exposure and risk assessments for the other dioxin **isomers**.

Since undertaking this research direction from the November 1983 "**Dioxin Strategy**", **EPA/ORD** has developed and implemented most of the programs to address these needs. As **expected**, the **scope** and priority of the component research projects have changed since November 1983. To provide a basis for updating the research program, current regulatory activity is discussed below.

CURRENT REGULATORY ACTIVITY FOR CDDs/CDFs

Provisions for the protection of human health and environment from adverse effects of CDDs/ CDFs are found in a number of environmental statutes. Regulations already issued by EPA in response to the statutory requirements of RCRA, FIFRA, and TSCA now control the generation, use, and disposal of many CDD/CDF-containing materials or precursors. There is much current activity related to the recent RCRA dioxin rule, including the delisting of residues from treatment of CDD/CDF wastes, the certification of incinerators to treat CDD/CDF-contaminated wastes and soils, development of special standards and guidance for land disposal and other treatment, storage, and disposal techniques for CDDs/CDFs. In addition, under the RCRA amendments of 1984, EPA is developing design and operating guidelines for municipal waste combustion facilities to minimize the formation and emissions of CDDs and CDFs. Concurrently, programs under TSCA (Sections 4 and 8) are proceeding to identify manufacturing products that may result in CDD/CDF exposures. Other regulatory programs also addressing CDDs/CDFs are Section 112 of the CAA (NESHAP) and CWA Section 307(a)(2). Additionally, the CERCLA (Superfund) program addresses sites where CDD/CDF contamination warrants immediate removal or remedial action.

CHAPTER IV

REGIONAL PERSPECTIVE

The **dioxin** problem has had an impact on every EPA region in the country.

- Region I has **PCB-contaminated** sites in Massachusetts and **Rhode Island**.
- Region II has **CDD/CDF-contaminated** sites in **Niagara Falls**, New York, and **Newark**, New Jersey.
- Region III has a **CDD-contaminated** site at Fort A. P. **Hill** and **PCB** transformers/capacitors in Maryland.
- Region IV has wood treating waste sludges in North **Carolina**, Georgia, and the USAF Site at **Gulfport**, Mississippi.
- Region V has **PCB** and **CDD/CDF-contaminated** waterways in **Indiana** and **Michigan**.
- Region VI has **CDD-contaminated** liquid wastes and soil at the vertac site in **Jacksonville**, Arkansas and **CDD-contaminated** soils in **Louisiana**.
- Region VII has 44 **CDD-contaminated** sites in Missouri.
- Region VIII has wood treating waste sludges in Montana.
- Region IX has twenty wood treating waste sludge sites in California; and the USAF site at the Johnston Island in the Pacific Ocean.
- Region X has wood treating waste sites in **Oregon** and Washington, and **CDD** contaminated soils in Oregon.

EPA regions V and VII have attracted much attention. The activities of these two regions are provided below in some detail.

Region V:

In the late 1970s, investigations in the **Great Lakes** area showed patterns of **2,3,7,8-TCDD** contamination in fish, herring gull eggs and other environmental media. **These** results were summarized in a July **1981** Region V report. As the most interesting results were the concentrations in **fish in** the **Tittabawasee** River, a number of field activities ensued, **including in 1981**, a wastewater and fish **bioaccumulation** study at Dow Chemical-Midland. These results helped lead to the issuance of an **NPDES** permit for **Dow in 1984**, and a number of **measures** by that company to reduce dioxin discharge to the river. A further and much larger investigation of the Midland area began in **1983**, on sediments and other media. Results of this study are now becoming available. The discovery of 2,3,7,8-TCDD at that site is the subject of a Consent Order.

Findings at Midland and elsewhere have contributed to the **now-familiar** 7 tiers of study of the Dioxin Strategy. Region V efforts parallel those occurring nationwide, although somewhat greater emphasis has been placed on dioxin and furan **isomers** other than **2,3,7,8-TCDD**.

Background soil **sampling** in connection with the Midland area studies showed no detectable dioxin in natural areas and much lower levels of dioxin than at Midland in two other industrial areas used for control. **2,3,7,8-TCDD** fish results are starting to **come** in and are being searched very closely for patterns, for example, at the sites downstream of **papermills**. The region has been involved in dioxin and furan contaminant monitoring **in fish** for several years, particularly in the Great Lakes Basin, and has **published a number** of reports; the most recent, a summary of dioxin and furan **fish** contaminant data, was published in October 1984. The large amount of furan contamination in Great Lakes Basin fish must be considered a **significant finding**.

Region VII:

In Missouri (Region VII), over 44 sites have been **identified** which are contaminated with **2,3,7,8-tetrachlorodibenzo-p-dioxin** at levels above one part per billion. Many of these sites resulted **from** the waste disposal practices of a now-defunct producer of **2,4,5-trichlorophenol** and **hexachlorophene**. Most of these sites **were identified** more than 10 years after the initial contamination. The high levels found at these sites attest to the **remarkable** stability and persistence of **2,3,7,8-TCDD** in the **soil** environment.

A number of options for remedial action have been proposed. These **include**: stabilization in place, **on-site** storage, transportation to a secure **landfill**, solvent extraction, biodegradation, chemical **degradation** in place, and **incineration**. The results of **this** evaluation and the **demonstration** of a mobile incineration system constitute major advances toward **detoxification** of dioxins. They are described in detail below.

The Mobile Incineration System was designed and built to provide onsite thermal destruction and **detoxification** of hazardous and toxic organic **substances**. The total system consists of: (1) major incineration and **air** pollution control equipment mounted on three **heavy-duty semi-trailers**; (2) combustion and stack gas monitoring equipment housed within a fourth trailer; and (3) ancillary support equipment.

In 1982, this incineration system successfully destroyed liquid organic carbon **tetrachloride**. Consequently, the system was granted **TSCA** and **RCRA** permits to burn liquid **PCBS** and **RCRA-designated liquids** having combustion heats equal to or greater than that of carbon tetrachloride. The primary purpose of the trial burn described here **is** to obtain data which verify that dioxins and other hazardous organic liquid and solid material **adequately** can be destroyed by incineration in this system, and that **the** resulting **stack** emissions do not pose a risk that is unacceptable to **the health** or **safety** of the surrounding communities. The trial burn **data** also support the issuance of the Federal and State permits **required for** extended use of the system at the **Denney** Farm site in southwestern Missouri.

EPA and State regulatory offices currently require trial burn data on both liquids and solids because of the processing **differences** between the two **in** the kiln of a kiln-plus-secondary combustion-chamber-type **incinerator**. **In part**, this is because organic liquids can **be passed** through a burner and **be** directly destroyed; whereas, solids are heated by **thermal** radiation and by contact with a refractory in a kiln.

Another objective of **the** program was to demonstrate that a **99.9999%** destruction and removal efficiency (**DRE**) could be achieved for incineration of **"dioxin"** wastes, since **this requirement became effective** on July 15, 1985. The **RCRA** and **TSCA** regulations both address the measurement of incinerator stack emissions as their primary performance criterion. The required **DRE** achieved by an incineration system under **TSCA** for **PCBs** is at least **99.9999%**; under **RCRA** for other hazardous materials, **it is** at least **99.99%**. A **DRE** of **99.9999%** or better is now required by **OSWER** for dioxins. The **DRE** is computed from the emission rate of hazardous materials in the incinerator stack and the feed rate of the material to the incinerator.

CHAPTER V

DIOXIN RESEARCH IN EPA

INTRODUCTION

In response to Congressional concern, the Agency established a **dioxin** research program to address critical issues related to environmental contamination **of**, and human exposure to, **dioxins** as a result of **chemical** production, incineration and waste disposal. The research was **initiated** during **FY 1984**, under the **framework** of the **Agency's "Dioxin Strategy"**.

The strategy identified five important questions and proposed plans to address each question. The questions dealt with: (1) sources, (2) **monitoring** and fate, (3) toxicity, (4) approach, and (5) abatement. In response to the first and second questions dealing with sources, monitoring, and fate the, strategy identified seven categories, or "tiers", of sites for dioxins. The third question was concerned with toxicity. The Agency proposed that ORD develop health and environmental assessment **profiles** and **define** their research needs. The fourth **question** addressed the approach for testing promising destruction techniques, once toxicity was established. The fifth question was concerned with abatement.

The strategy **specifically** charged ORD with the **following** tasks: (1) Pilot testing of the more promising disposal/destruction techniques including a **comprehensive** study of binding of **dioxins** to soils and field validation of the destruction techniques; (2) Guidance in sampling, and analytical **methods** for detection and **quantification** including quality assurance; (3) Conducting hazard and exposure assessment for **site-specific** risk assessments including establishing exposure scenarios; and (4) Evaluation of the **bioavailability** or dioxins for use in food chain **models**.

During the initial stages in **developing** the research program, the Agency considered the following critical issues: (1) The **availability** of analytical methodologies and in-house capability to identify and quantify dioxins in environmental media; (2) Evaluation of existing control technologies for destruction of dioxins plus clean-up sites; and (3) An assessment of both the **bioavailability** of, and the human exposure from, dioxins in contaminated soils.

In support of the strategy, the Agency began **its** research program focusing on the most toxic **isomer, 2,3,7,8-TCDD**, but the scope of research has expanded to include other **isomers** and related compounds such as **chlorinated dibenzofurans**.

RESEARCH ORGANIZATION AND BUDGET

The EPA research on dioxins is organized **into** four areas. These are technology assessment, **monitoring**, environmental **effects**, and **health** assessment. The broad objectives of each research area are **defined** below:

Technology Assessment

This program is to evaluate the available technologies and **develop** new technologies for **detoxification**, destruction or control of dioxin-**contaminated** materials.

Monitoring

Research under this program is devoted to developing **measurement** methods and quality assurance procedures for identifying and quantifying dioxins in environmental samples and biological matrices.

Environmental Effects

The objectives of the environmental research are to evaluate the fate and effects of dioxins in the environment, and to determine the uptake and **bioavailability** in plants and living systems.

Health Assessment

The objectives of the health assessment research are to develop **methodologies** and the necessary data base for evaluating human health exposure and risks associated with dioxins, and provide to the Agency the information necessary to perform exposure and risk analyses.

The EPA laboratories participating in each of the above areas of research are given in Table I.

TABLE I

EPA LABORATORIES PARTICIPATING IN DIOXIN
RESEARCH

<u>RESEARCH AREA</u>	<u>EPA LABORATORY</u>
Technology Assessment	Hazardous Waste Engineering Research Laboratory (HWERL-Cinn.) Cincinnati, Ohio
Monitoring	Environmental Monitoring and Systems Laboratory (EMSL-LV) Las Vegas, Nevada
	Environmental Monitoring and Systems Laboratory (EMSL-RTP) Research Triangle Park, North Carolina
	* Environmental Chemistry Laboratory (ECL-Bay St. Louis) Bay St. Louis, Mississippi
	Environmental Monitoring and Systems Laboratory (EMSL-Cinn.) Cincinnati, Ohio
Environmental Effects	Environmental Research Laboratory (ERL-Duluth) Duluth, Minnesota
	Environmental Research Laboratory (ERL-Corvallis) Corvallis, Oregon
	R. S. Kerr Environmental Research Laboratory (RSKERL-Ada) Ada, Oklahoma
	Environmental Research Laboratory (ERL-Athens) Athens, Georgia
Health Assessment	Health Effects Research Laboratory (HERL-RTP) Research Triangle Park, North Carolina
	Environmental Criteria and Assessment Office (ECAO-Cinn.) Cincinnati, Ohio

*This laboratory is part of the **Office** of Pesticides and Toxic Substances in EPA.

The dioxin research budgets for FY'84 and FY'85 were about \$2.4 million and \$3.0 million, respectively. For FY'86, the Agency's proposed budget is approximately \$3.7 million.

The breakdown of the resources in each area of research are found in Table 2.

TABLE 2
DIOXIN RESEARCH FUNDING

RESEARCH AREA	RESOURCES (\$ in 1,000)		
	1984	1985	(Proposed) 1986
Technology Assessment	998	1,269	1,030
Monitoring	570	725	725
Environmental Effects	466	531	1,242
Health Assessment	<u>351</u>	<u>450</u>	<u>736</u>
Total	<u>2,385</u>	<u>2,975</u>	<u>3,733</u>

In addition to the above resources the Agency contributed \$2.4 million in FY'84 and \$2.0 million in FY'85 from "Superfund" to accelerate the engineering evaluation program. These resources were used specifically in that program, and to augment ORD resources for the evaluation of the mobile incinerator in Missouri, as "Superfund" resources can only be used for ~~site-specific~~ purposes.

MAJOR ACCOMPLISHMENTS

Initial studies within this research program have provided the following information which is critical to the dioxin issue:

TECHNOLOGY ASSESSMENT

Work on detoxification of dioxin-contaminated soils using ultraviolet (UV) photolysis in conjunction with alkali polyethylene glycolate (APEG) reagents is continuing at a contaminated site in Missouri. If promising, this treatment will be extended and enlarged in a full field evaluation of the technique.

The Agency has devoted considerable effort to developing and improving incineration techniques for destruction of dioxins. Field testing of the EPA mobile incineration system is continuing. Trial burns were conducted in 1983 in Edison, New Jersey on RCRA listed surrogates. Currently, the incinerator is installed at the Denney Farm site near McDowell, Missouri. Data from four recent trial burns using dioxin-contaminated liquid wastes and soils have established the DRE at greater than 99.9999%, and have verified the effectiveness of control devices.

The white rot fungus, Phanerochaete chrysosporium, has been found to degrade 2,3,7,8-TCDD, DDT, lindane, PCBs, and other recalcitrant halogenated organics in laboratory experiments. Field testing will be the next step in evaluating feasibility for dioxin degradation using this microbe.

MONITORING

Through a collaborative effort of three EPA laboratories (ERL-Duluth, EMSL-RTP, and ECL-Bay St. Louis), the Agency has developed a network known as TROIKA to provide analytical support in identifying and quantifying parts per trillion (ppt) levels of dioxins in environmental samples to support the National Dioxin Strategy. This was necessary because of the prior lack of analytical capability to routinely analyze large numbers of samples. Through the establishment of TROIKA the Agency has significantly improved its capability to analyze dioxins in environmental samples and hazardous waste site samples. TROIKA has provided analytical support to Region V, by analyzing environmental samples in the Midland study and has also analyzed samples for the States of Michigan and Wisconsin.

Significant progress has been made through the Agency contract laboratory program in developing analytical methods and quality assurance materials to ensure routine ppt analyses of dioxins in environmental samples. A high resolution gas chromatography and mass-spectrometry (GC/MS) method to analyze dioxins in environmental matrices at trace levels has been developed and evaluated. A round-robin validation study is being conducted in various laboratories where such validated methods will be used routinely in the future.

Additionally, a pilot round-robin survey of trace analyses of "dioxins" and furans in adipose tissues was conducted. The results show that parts-per-trillion analyses of dioxins in adipose tissue may be made on a routine basis.

The monitoring program provides quality assurance in analyzing dioxins. An interim quality assurance document for analyzing 2,3,7,8-TCDD was produced in FY'84 for use in the National Dioxin Study. Reference isomers for tetra dioxin analysis were produced. Quality assurance efforts are underway through contract laboratory work with the Centers for Disease Control. Quality assurance is being provided to the TROIKA for the National Dioxin Study and for the mobile incinerator demonstration. Specific focus is on review of a procedure to collect and analyze combustion samples, review of quality assurance plans and analytical methods used, and corrective measures taken to maintain data quality.

ENVIRONMENTAL EFFECTS

A national workshop on bioavailability of dioxins was held in Raleigh, North Carolina in September 1984. Scientists from academia, industry and government met and identified research needs in this area. The findings are being used to refine future research planning. This includes initiation of new research projects as well as refocusing of certain ongoing projects.

A bioavailability study using laboratory animals exposed to contaminated soils from sites in Missouri, New Jersey, and Seveso, Italy is under way at the University of Medicine and Dentistry of New Jersey (UMDNJ). This study is a follow-up to studies at the National Institute of Environmental Health Sciences dealing with the dependency of the bioavailability of dioxins from soils, on the nature of those soils, and on other environmental conditions. The bioavailability of New Jersey soil compared to Missouri soil was negligible in laboratory test animals.

Laboratory experiments to determine the sorption/desorption characteristics of 2,3,7,8-TCDD in contaminated soils from Missouri and New Jersey are complete. The data indicates that, for practical purposes, the 2,3,7,8-TCDD would be essentially immobile in water percolating through the soils. Studies of dioxins from municipal incinerator fly ash have also been completed. These studies have shown that 2,3,7,8-TCDD selectively bioaccumulated in carp fish when the fish were exposed to municipal incinerator fly ash. This work will appear in "Chemosphere". Similar exposure studies with other isomeric TCDDs (1,2,3,4; 1,2,6,8; 1,3,7,9; and 2,3,7,8) in carp and fathead minnow are in progress. Dioxin bioavailability data from Petenwell Reservoir on the Wisconsin River are being used to investigate sediment-mediated exposure to fish, and the resulting uptake, bioaccumulation and depuration.

HEALTH ASSESSMENT

A document describing the assessment methodologies used by EPA in evaluating 2,3,7,8-TCDD health hazards has been completed. It is being updated to include a comparison of risk assessment methods used by other organizations.

Assessment methods for evaluating exposure to humans from dioxin-contaminated soils have been developed. Five major pathways for exposure have been identified, and nomographs have been provided for each of these pathways to permit a quick approximation of upperbound risk for exposed persons.

In collaboration with NIOSH, registry data is being developed to include work history information for U.S. production workers who are potentially exposed to dioxins during the synthesis or formulation of substances containing dioxins. Thirteen sites have been included in the registry and about 6,000 workers have been identified. "Supertund" resources support this project.

Pharmacokinetics studies with rhesus monkeys have provided sane results. Tissue samples of monkeys exposed to 2,3,7,8-TCDD at 0.25 ppt and 25 ppt in their diet are being analyzed. Preliminary results show that bone marrow and axial lymph nodes have higher levels of TCDD than other tissues. The tissue of one animal that gave birth, nursed and weaned her offspring during the latter period of exposure had non-detectable levels of TCDD in her tissues. However, additional efforts must be made to confirm these findings. Furthermore, tissues from a stillborn of an exposed mother are currently being analyzed.

The half-life for 2,3,7,8-TCDD in monkeys is being determined and will be the first such determination in primates for low levels of exposure over a long period of time.

Preliminary findings suggest that monkeys previously exposed to 2,3,7,8-TCDD gave normal numbers of live births, birth weights, and weaning weights as compared to those animals that gave birth while being exposed to dioxins. However, the number of animals used in these studies was small and there may have been a bias in the selection of animals. Therefore, the studies must be confirmed. Lymphocyte studies are being conducted to measure for gene mutations and immunotoxic effects caused by 2,3,7,8-TCDD.

DESCRIPTION OF RESEARCH PROJECTS

A description of the overall program and projects conducted under the four major research areas follows.

TECHNOLOGY ASSESSMENT RESEARCH

The objectives of this research program are: (1) to conduct basic and applied research on the behavior of 2,3,7,8-TCDD in contaminated soils, applying this knowledge to methods useful in the in-situ stabilization of such soils, and investigating the viability of special microorganisms or chemical reagents for the destruction of TCDD and related toxic chemicals; (2) to develop information on the generation of dioxins and furans from PCBs in transformers and capacitors when thermally stressed; and (3) to develop and evaluate, both in the laboratory and in the field, technologies for the detoxification, destruction, or control of 2,3,7,8-TCDD-contaminated liquids and soils.

Descriptions of technology assessment research projects follow.

PROJECT I

TITLE: In-situ Stabilization Techniques

CONTACT: Don Sanning, HWERL-Cincinnati, Ohio

OBJECTIVES: The objectives of this investigation are: (1) to evaluate cost-effective fixation or stabilization techniques that can be used to immobilize dioxin-contaminated soils and serve as a needed initial remedial measure (IRM) technology for dioxin-contaminated soils; (2) to evaluate these stabilization techniques in the laboratory so as to develop optimum soil/stabilizer proportions and mixing conditions using industry standardization protocols and acceptance criteria; and (3) to assess the probability of successful field implementation of these methodologies through evaluation of the ability of weathered, stabilized soil mixtures to inhibit transport of these soils.

BACKGROUND/RATIONALE: Under the January 14, 1985 dioxin listing rule, dioxin-contaminated soils have been classified as acute hazardous wastes that require special management to prevent migration and reduce human exposure. At this time, a control technology is needed to prevent adsorption and transport of dioxin from soil particles by either precipitation or wind.

CURRENT STATUS: Three Missouri sites were selected for evaluation of the feasibility of cement and asphalt stabilization techniques: (1) Minker site - a residential area with steep, sloping banks that drain into a nearby creek (TCDD = 700 ppb/sandy loam); (2) Piazza Road - a roadside material (TCDD = 640 ppb/sandy loam); and (3) Sontag Road - a roadside material but with a considerably greater percentage of fine particles (silt and clay) (TCDD = 32 ppb/sandy silty loam).

Cement specimens were formulated at optimum moisture, but with varying cement contents, and tested for freeze/thaw susceptibility, and 7-day unconfined, comprehensive strength. Significant quantities of specimen loss occurred during the two sequential weathering processes, followed by the aqueous leaching procedure. Percent-by-weight degradation of the solid soil/cement specimens into disassociated particles ranged from 6-to-18% for Minker, 13-to-16% for Piazza Road, and 16-to-27% for Sontag Road, under the rigorous laboratory procedures employed.

Differences in settling rates between soil/cement disassociated particles and native, unstabilized soil observed during the leaching process, suggest that the former contain a very low percentage of "erodable" silt and clay-sized particles (<50 um diameter).

For the emulsified asphalt stabilization tests, a cationic, **slow-setting** emulsion (**CSS-1h**) was chosen as the grade of asphalt to be used because a low-setting emulsion is **recommended** for **mixed-in-place** applications when a **dense-graded** aggregate is encountered, such as in Missouri soils. After mix design work was **completed** on **Minker** and **Piazza Road** sites, it became apparent that **emulsified** asphalt per se would not provide an effective method for stabilization of the test soils.

As a result, **calcitic lime**, calcium hydroxide, was employed to modify the soil prior to asphalt **addition**, thus reducing the effective **surface** area of the soil to be coated, and the subsequent reduction in swell characteristics improved the properties of the compacted soil/asphalt mixtures exposed to water. Curing or **pozzolanic** action took place within the soil and contributed additional strength to the soil/asphalt matrix. Therefore, addition of 1.5% lime dramatically improved the performance of soil/asphalt specimens when the **SS-1h**, a nonionic, **slow-setting** emulsion, was substituted for the **CSS-1h** emulsified asphalt previously employed.

FUTURE DIRECTIONS: Nine percent residual asphalt (RA) was chosen as the optimum asphalt percentage, which includes a safety factor of 0.5% RA. In addition to compacted **specimens** for each soil, triplicate **soil/asphalt/lime** mixtures from the Minker site **were** formulated but left **uncompacted** to evaluate the leaching potential and acceptability or **this alternative**. This option is currently being investigated because a keen interest has been expressed to evaluate an option in which a temporary **in-situ** stabilization effort is subsequently followed by **soil/ stabilizer removal** and thorough stabilization at an off-site facility. Particle size analyses on **uncompacted** mixtures as well as non-associated particles **from** compacted specimens are awaiting **completion**.

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PROJECT II

TITLE; White Rot Fungus: Phanerochaete chrysosporium

CONTACT: Pat Sferra, HWERL-Cincinnati, Ohio

OBJECTIVES: The basic objective of **biodegradation** research is to identify, develop and test microorganisms capable of degrading highly toxic and refractory **organohalide** pollutants, specifically **2,3,7,8-TCDD-contaminated sites**.

BACKGROUND/RATIONALE: Biotreatment systems using microorganisms for the degradation of toxic and refractory **organopollutants** hold the promise of being an **efficient** and economical means of detoxifying contaminated water, soils and sediments. Few organisms, **however**, have shown the ability to degrade organohalide pollutants. In general, organohalides are poorly soluble in water and are **sorbed** to **particulate** matter, thus making them even less susceptible to microbial attack. Pollutants of interest (i.e., **2,3,7,8-TCDD**) are often present in the parts per million range or less.

Microbial enzymes, which may be able to degrade organohalide pollutants, however, do not function effectively at **the** very low **substrate** concentrations. Microbial strains especially adapted to grow on organohalide pollutants have only shown limited effectiveness. Because the chemical substances are present in such low **concentrations**, these strains may not be able to compete effectively with other microorganisms in a **biotreatment** system.

CURRENT STATUS: Research performed over the last nine years has not yet produced biodegrading organisms suitable **for** **detoxification** of 2,3,7,8-TCDD. Recent interest, **however**, has focused on a unique hydrogen **peroxide-dependent** oxidase secreted by the white rot fungus, *Phanerochaete chrysosporium*. **P. chrysosporium** and related fungi (there are 1,600-1,700 species of wood-rotting fungi in the class **Basidiomycetes**) have the ability to recycle carbon bound within lignin.

This enzyme system has proven effective in degrading lignin, a highly complex, chemically resistant, nonrepeating **heteropolymer**. In cultures (10 ml) containing 1.25 **nmoles** of the carbon labelled 2,3,7,8-TCDD substrate, 27.9 **pmoles** were converted to "**CO₂**" in 30 days (2.23% metabolism) increasing to 49.5 **pmoles** in 60 days (3.96% metabolism). Similar, but even more effective results were observed with other organohalides including lindane; **DDT**; **3,4,3',4'-tetrachlorobiphenyl**; **2,4,5,2',4',5'-hexachlorobiphenyl**; **4,5,6-trichlorophenol**; **3,4,5,6-tetrachloroquaiacol** and **2,4,6-trichlorophenol**.

The **P. chrysosporium** enzyme system may prove to **be** **ideally** suited for use in biotreatment processes for the degradation of recalcitrant **organopollutants**: First, the enzyme system normally attacks an insoluble recalcitrant substrate. Thus, organopollutants adsorbed to sediments may actually mimic the lignin molecule. The analogy is even more **striking** when one **considers** that many sediments and soils to which organopollutants are adsorbed have high lignin contents.

Second, problems associated with substrate specificity appear to be obviated by the non-specific and **non-stereoselective carbon-centered**, free radical mechanism that is characteristic of this system. This lack of **specificity** has the advantage of allowing the organism to attack and degrade a broad spectrum of structurally diverse recalcitrant compounds.

Third, **P. chrysosporium** is a highly successful competitor in nature, especially when the carbon source consists of **wood**, **wood by-products** or other lignin containing materials. Thus, if wood chips or **sawdust**, for example, are used as the carbon source in **biotreatment** systems, competition by **non-lignin** degrading organisms is likely to be minimal.

Fourth, because degradation is **promoted** by nitrogen starvation rather than by the presence of substrate, low levels of organopollutants do not repress the biosynthesis of enzymes required for their **degradation**. **Fifth**, the carbon-centered radical mechanism appears to provide an alternative mechanism that allows degradation of lignin, and possibly other recalcitrant compounds, to proceed to completion.

Of special significance for the degradation of **organohalides** is the fact that **P. chrysosporium** has the demonstrated **ability** to **dehalogenate** and degrade **chlorobenzene derivatives** and to cleave aromatic rings.

FUTURE DIRECTIONS: The **P. chrysosporium** enzyme system will be **field tested** in a small number of plots during the summer of 1985 at one of the contaminated sites in Missouri. These experiments may be considered as extensions of **the** ideally conducted tests in the laboratory and may indicate whether a full field evaluation is justified next summer.

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PROJECT III

TITLE: Shallow Mines as Repositories for **Dioxin-Contaminated** Soils

CONTACT: Janet Houthoofd, **HWERL-Cincinnati**, Ohio

OBJECTIVES: To evaluate the feasibility of utilizing abandoned mines located in or near Missouri as repositories for **dioxin-contaminated** soils.

BACKGROUND/RATIONALE: The state of Missouri contains a large number of underground mines of various types, including shallow and deep, active and inactive, **limestone, sandstone,** lead, and iron varieties. If contaminated soil is removed from the numerous **dioxin** sites in Missouri during remedial action cleanup operations, certain abandoned mines have a potential to be used as secure facilities for the placement of contaminated material.

It is assumed that it would not be necessary to subject the dioxin-contaminated soil to a stabilization process before placement in a mine because research on the **desorption** characteristics of **2,3,7,8-TCDD** has shown it to be essentially **non-mobile** (mean value based on partition **coefficient** determination--400 **yrs/cm**). However, some type of containment would be necessary (**i.e.**, steel vaults, barrels, or polypropylene bags).

CURRENT STATUS: The types of mines available in Missouri have **been investigated**. Twenty nine mines, ranging in physical condition from abandoned and collapsing to excellent warehouse quality, were selected for study and 20 of these sites were visited. Aerial reconnaissance of **mine** sites was performed. Geological and **hydrogeological** conditions were extensively reviewed. The Missouri Department of Natural Resources, the University of Missouri (**Rolla**) School of Mines, and EPA Region VII staff were involved in the project from its onset.

Specific selection criteria were employed to determine which mines would be considered for review and evaluation. These included: (1) Isolation from the surface environment and human contact; (2) Reduction in the likelihood of inadvertent intrusion; (3) Adequate confinement from secondary leakage problems; (4) Surroundings that were chemically compatible with and thus would not corrode the waste forms or containers; (5) Disposal areas that could easily be accessed for reconditioning and monitoring; (6) Location above the local water table to prevent flooding and **groundwater** intrusion; (7) Those mines located within a reasonable distance to problem areas; (8) Selection limited to only mines already known to the Missouri Department of Natural Resources, Division of Geology and Land Survey.

Based on these criteria, 29 mines were investigated. Shallow, underground **limestone/dolostone** mines were found to offer distinct technical advantages over all other types of underground mines, for example, sandstone, lead zinc, **iron,** and coal. These advantages principally are related to **dryness,** structural stability, potential size, location, and accessibility factors.

The overall cost of developing a **facility** was found to be affected primarily by the contaminated soil packaging container and **mine packing** arrangement. The packaging options evaluated included rectangular steel vaults, steel drums, and woven propylene sacks. **Supersacks** are considerably less expensive than metal drums (plastic drums were not used in cost **estimates**), and metal drums are less expensive than metal vaults. **Supersacks** allow more soil to be stored in the same available space than the other packaging systems. **Three** different spatial arrangements for packing the containers **in** mines were also evaluated.

FUTURE DIRECTIONS: The project will expand beyond the concept of using existing mines to explore the concept of **developing** a new mine for storage purposes. Development of a new mine for storage purposes **compared favorably with** rehabilitation of an existing, inactive mine. Per unit ton costs for **dioxin-contaminated** soil will be developed and **compared** to excavation, **containerization**, and interim storage **in** pole Dams.

REFERENCES:

"Feasibility of Utilizing Mined Space in Missouri for Long-term Placement of **Dioxin-Contaminated Soils.**" Internal draft report prepared by PEI Associates, Inc., for EPA. EPA Contract No. 68-02-3963, Work Assignment No. 9, May 9, 1985.

Fortunati, G.U. "The Seveso Lessons: Advances in Reclamation And Disposal Techniques." Region Lombardia, Ufficio Speciale, Seveso (Milan), Italy (1985).

PROJECT IV

TITLE: Mobile Incineration

CONTACT: Frank Freestone, HWERL-Cincinnati, Ohio

OBJECTIVES: the **OBJECTIVES** of this research and evaluation program were: (1) to improve and facilitate the permitting process; (2) to establish that permit conditions of 99.9999% **DRE** and delisting guidelines for **dioxins** and other hazardous waste components could consistently and **reliably** be met; (3) to develop **site-specific** risk assessment methods; (4) to **document the economics** of the process; (5) to develop and put into practice an **aggressive and positive** community relations program; and (6) to demonstrate to the public that **dioxin-containing** wastes and **dioxin-contaminated** soils could be safely processed and thereby open the marketplace to the private sector for use of **equivalently** effective technologies.

BACKGROUND/RATIONALE : As a result of the verification of 44 **dioxin-contaminated** sites within the State of Missouri, the need arose to initiate a field evaluation of a thermal destruction process **sufficiently** advanced and laboratory tested that would, in effect, be capable of **achieving** a **DRE** of 99.9999%, and hence be able to remediate a significant number of these sites.

CURRENT STATUS: In 1983, trial burns were conducted in Edison, New Jersey on RCRA-listed surrogates, including dichlorobenzene, trichlorobenzene, tetrachlorobenzene, Aroclor 1260, and tetrachloromethane (CCl₄). After a solids feed system was installed and tested in December 1984, additional laboratory tests were conducted by the IT Corporation in Knoxville, Tennessee. Currently, the mobile incinerator is installed at the Denney Farm site near McDowell, Missouri, where "cold" and "hot" tests were conducted using clean soil and soil contaminated with surrogates similar to those employed in the earlier liquid waste tests (CCl₄ and hexachloroethane). Tests using dioxin-contaminated liquid wastes and soil verified the DRE and the effectiveness of the control devices. Interim delisting guidelines were established and analyses were conducted on ash, treated soils, filter materials, and process/quench water to ascertain if the guidelines were attainable.

Results of the four recently completed dioxin test burns were compiled from more than 15,000 pages of analytical data and reviewed for quality assurance/control by EMSL IV.

The dioxin trial burns were successful with DREs exceeding 99.9999%. During these tests 3.84 pounds of 2,3,7,8-TCDD, contained in 1,750 gallons of liquids and over 40 tons of soil, were destroyed. Particulate emission permit limitations (<180 mg/Nm³ @ 7% O₂) were achieved in three of four test runs. The fourth run exceeded the prescribed limit slightly, possibly due to the accumulation of submicron-sized particles in the air pollution control system. The observed CO emission values (1.3-7.7 ppm) are equivalent to those from the best available incineration technologies and are indicative of very complete combustion (C.E.s = 99.993 - 99.999%).

Finally, the treated soil (ash) and process wastewater from the trial burn were analyzed for a series of specific constituents considered as likely contaminants. The results of these analyses were used to support an application to "delist" residues from a planned larger scale burn of similar wastes.

FUTURE DIRECTIONS: ORD currently is preparing to conduct three experimental test burns later this summer at its Combustion Research Facility (CRF) near Pine Bluff, Arkansas. The three wastes to be investigated include OCC Hyde Park NAPL, Vertac still bottoms (Jacksonville, AR.), and TVA, Muscle Shoals, AL, Herbicide Orange. The three test burns will generate invaluable combustion data that will be useful in obtaining EPA licensing for mobile or transportable incineration units.

Additional research may be conducted using a variety of composite sludges from wood treating waste lagoons containing creosote, pentachlorophenol, dioxins, furans, copper and zinc naphthalenates and arsenicals, inorganics, etc.

REFERENCES:

Yezzi, J.J., Jr., Brugger, J.E., Wilder, I., Freestone, F., Miller, R.A., Pfrommer, C., Jr. and Lovell, R. "Results of the Initial Trial Burn of the EPA-ORD Mobile Incineration System." Proceedings of the 1984 National Waste Processing Conference, Engineering: The Solution, ASME, New York, NY, pp. 514-534 (1984).

"Dioxin Trial Burn Data Package: EPA Mobile Incineration System at the James Denney Farm Site, McDowell, Missouri." Prepared by IT Corporation for EPA HWERL-Cincinnati, EPA Contract No. 68-03-3069, June 21, 1985.

PROJECT v

TITLE: UV Photolysis/APEG Chemical Detoxification

CONTACT: Charles Rogers, HWERL-Cincinnati, Ohio

OBJECTIVES: The ultimate objective of the APEG program is to develop reliable and cost-effective techniques for the destruction and/or detoxification of toxic halogenated organics, including 2,3,7,8-TCDD, present in contaminated soils at dumpsites and in roadbeds and horse arenas that have been coated with dioxin-containing waste oils. The specific objective is to determine the degree of effectiveness of APEG reagents singly and in conjunction with UV irradiation at ambient conditions in the field.

BACKGROUND/RATIONALE: Chemical destruction of dioxins within Missouri soils may represent a practical method for reducing widespread contamination. Laboratory tests, conducted at EPA HWERL Cincinnati, have shown the ability of newly developed chemical agents termed APEGs to destroy 2,3,7,8-TCDD in solution and within a limited number of contaminated Missouri soils.

CURRENT STATUS: Laboratory proof-of-principle experiments using 1,2,3,4-TCDD show that this isomer in soil may be chemically dechlorinated to levels below 1 ppb in soil. The dechlorination is accomplished by addition of APEG reagents (in some instances, dimethyl sulfoxide [DMSO]) to the soil allowing the reagent mixture to extract and dechlorinate the 1,2,3,4-TCDD at temperatures from 70-170°C. Three methods of application are currently under investigation in the laboratory: in-situ, heated in-situ, and slurry; the latter involving reagent recovery and recycle.

Currently, a technical team is planning to conduct field experiments at a specified site in Missouri. At least two **in-situ** techniques for applying APEG reagent to **dioxin-contaminated** soil will be evaluated. A comparison will be made of single versus repeated application of APEG in the reduction of **TCDD** levels. A field trial involving three treatment levels, to be carried out on **4' x 4'** soil **plots**, will be designed according to the Latin Squares experimental matrix. Treatment levels will include: (1) APEG on **soil**, covered by black polyethylene (to enhance and retain solar **heat**); (2) Polyethylene glycol in **soil**, uncovered (to evaluate photochemical processes); and (3) No treatment (to serve as **control**).

Costs of chemicals (APEG) are estimated \$1000/acre/1 cm penetration. Capital costs for a 160 **yd³/day** slurry process with reagent recovery are estimated at \$2.25 million, including \$0.75 million for an onsite **GC/MS/MS** trailer unit. Given these preliminary estimates and the fact that field evaluation tests must be conducted, it appears that applicability of this technique is limited to open, flat areas similar to dioxin-contaminated horse arenas, where minimal vegetation exists.

Data from soil borings at Times Beach, Missouri, demonstrate almost complete adsorption of **2,3,7,8-TCDD** within the upper 23 **cm** soil thickness and an interesting **chromatographic** effect when concentration of 2,3,7,8-TCDD (143 to 2 ppb **range**) is plotted against soil depth. Total organic carbon (**TOC**) (117 to 6 **ppm** range) adsorption paralleled that of TCDD except that removal occurred in the upper 5 **cm**. Given this information, chemical **detoxification** of contaminated soils will be limited by depth of penetration. In other words, the upper 30 **cm** (12 in.) soil thickness is the depth of concern and detoxification will be limited to that **depth**. Any remaining TCDD below this depth is assumed to be **immobile**.

FUTURE DIRECTIONS: Phase **I--current test program--will** continue through the fall of 1985, If deemed **successful**, Phase **II--a thorough site treatment and detoxification--will** commence in the summer of 1986 and continue through the fall of 1986.

REFERENCES:

Peterson, R.L., Milicic, E., and Rogers, C.J. "Chemical Destruction/Detoxification of Chlorinated Dioxins in Contaminated Soils," Paper presented at the EPA **HWERL 11th** Annual Research Symposium, Cincinnati, OH, April 29-May 1, 1985.

Dev, H., Bridges, J.E. and Sresty, G.C. "Decontamination of Hazardous Waste Substances from Spills and Uncontrolled Waste Sites by Radio Frequency **In-Situ** Heating." 1984 Hazardous Material Spills Conference Proceedings, Nashville, **TN**, April 9-12, 1984.

"Times Beach Soil Core Analyses." Memorandum of May 25, 1983 from J.D. Wilson, State of Missouri Department Natural Resources, to G. Roush, M.D.

U.S. Patent 4,353,793 (D.J. Brunelle, General Electric Co.), 12 October 1982.

Peterson, R. and Milicic, E, "Chemical **Destruction/Detoxification** of Chlorinated Dioxins in Contaminated Soils." **Summary** Report prepared for EPA **HWERL-Cincinnati** and **USAF Engineering and Services Laboratory**, EPA Contract No. 68-13-3219, June 26, 1985.

White, **J.B.**, **Leese**, K.E. and Clayton, **A.C.** "Interim Report on the Feasibility of Using U.V. Photolysis and APEG Reagent for Treatment of Dioxin Contaminated Soils." Final Report submitted to EPA **HWERL-Cincinnati** by Research Triangle Institute, EPA Contract No. 68-03-3149, June 1985.

PROJECT VI

TITLE: Assessment of PCB Transformer/Capacitor Fires

CONTACT: Brian Westfall, **HWERL-Cincinnati**, Ohio

OBJECTIVES: The objectives on this project were to assess the chemistry of PCBs under thermal conditions, evaluate the generation of PCDDs and PCDFs, and review emergency response procedures and remedial measures applicable to facilities contaminated by PCBs in fire incidents.

BACKGROUND/RATIONALE: The finding of PCDFs and potential generation of PCDDs from PCBs under stressed thermal conditions has major implications for mitigating and controlling chlorinated dioxins and furans in the environment. Findings of such toxic chemicals also complicate emergency response and cleanup procedures for fires involving PCBs-containing transformers and capacitors.

CURRENT STATUS: A final peer-reviewed report was prepared on schedule and covered three major areas: (1) the chemistry of PCB fires including theoretical products of thermal stress based on composition of the askarel used; (2) evaluation of emergency response procedures used by firemen, including protective clothing; and (3) evaluation of remedial measures for facility cleanup.

FUTURE DIRECTIONS: FY 85 research plans call for analyses of several PCB transformer/capacitor fluids involved in fire incidents in order to attempt to correlate PCDDs and PCDFs content of soot with chlorobenzene and PCB content in the askarel fluids. The information gathered, after internal Agency peer reviews, will be shared among the electric utilities, insurers, firemen associations, the Electric Power Research Institute (EPRI), NIOSH, and other concerned groups.

REFERENCES:

"Assessment of PCDDs and PCDFs from PCB Transformer and Capacitor Fires." Technical Resources, Inc., EPA Contract No. 68-03-3213, **HWERL-Cincinnati**, 118 pp. (1984).

MONITORING RESEARCH

The main thrust of monitoring research is to produce standardized analytical procedures to detect and measure chlorinated dibenzo-p-dioxins in environmental samples, and to establish quality assurance procedures to support their routine use.

Quality assurance support emphasized production of analytical reference isomers in milligram quantities. Wright State University produced the 22 tetra isomers of CDD. EMSL-LV evaluated their purity, dispensed them into aliquots and made them available for routine use. EMSL-LV has focused on production of key reference isomers for other dioxin homologues and for dibenzofurans with CDC. Together they will develop a standardized approach for production, purification, and distribution for research and routine monitoring. Once these compounds are produced, the method used for 2,3,7,8-TCDD analysis will be modified to demonstrate reliability of current analytical isomers and procedures to identify and to quantitate dibenzofuran isomers and for higher homologues of dioxin.

Brief outlines of the projects conducted as part of monitoring research follow.

PROJECT I

TITLE: Methods Development for 2,3,7,8-TCDD

CONTACT: Ron Mitchum, EMSL, Las Vegas, Nevada

OBJECTIVES: Produce a standard high and low resolution gas chromatography - high resolution mass spectrometry (HR/GC/HRMS) method to analyze 2,3,7,8-TCDD at parts per billion and parts per trillion levels in environmental matrices. Produce quality assurance reagents and guidelines to support routine trace analysis for 2,3,7,8-TCDD.

BACKGROUND/RATIONALE:

CURRENT STATUS: Wright State University produced an analytical method for EMSL-LV. EMSL-LV incorporated this, as the Region VII methodology, into a protocol and is testing the reproductibility and reliability of this method to detect trace levels of 2,3,7,8-TCDD in environmental media.

Wright State University produced the 22 tetra isomers for use in the quality assurance program. EMSL-LV verified their purity and distributed aliquots for routine use in the Agency's contract laboratory program. Efforts are underway at EMSL-LV to produce key reference standards for other dioxin homologues with CDC.

EMSL-LV produced an interim QA guidance manual in FY'84 which served as the source document for the TROIKA's program plan and QA program. This document will be completed in 1985 to serve the Agency's contract laboratory program.

FUTURE DIRECTIONS; EMSL-LV will investigate trace analysis of chlorinated dibenzo-p-dioxins and other complex organic compounds in adipose tissue, blood and human milk as part of human exposure monitoring research. Production of QA requests and QA guidance will be provided as research support to OSWER.

REFERENCES:

Analytical Protocol for Quantification of 2,3,7,8-TCDD and Total TCDD Present in Soil and Sediment Using High Resolution GC/MS. Prepared by Brehm Laboratory Wright State University, Dayton, Ohio, P.O. Stephen Billits, EMSL-LV. (Date?)

"Sane Analytical Considerations for the U.S. EPA High Resolution Mass Spectrometric Dioxin Analysis Protocol", Chopterm Chlorinated Dioxins and Dibenzofurans on the total Environmental III, in press.

Status Report: Quality Assurance Procedures for Chlorinated Dioxin and Dibenzofuran Analysis, J. R. Donnelly LEMSCO, Las Vegas, NV, P.O. J.G. Pearson EMSL-LV. (Date ?)

PROJECT II

TITLE: Methods Development - Round-Robin Survey for Adipose Tissue Analysis

CONTACTS: Michael Dellarco, EPA Headquarters, Washington, D. C.

OBJECTIVES: Obtain preliminary indication of differences which may exist among various approaches used to detect 2,3,7,8-TCDD. This would be accomplished through a round-robin survey of trace analysis of adipose tissue spiked with key dioxin and furan isomers.

BACKGROUND/RATIONALE: Determine if there are advantages to using different trace analytical methods for trace dioxin analysis and if efforts should be made to produce a single, validated standard method for trace analyses of 2,3,7,8-TCDD.

CURRENT STATUS: This project was completed in FY'84. Eleven of the leading international laboratories capable of measuring parts per trillion levels of chlorinated dibenzo-p-dioxin in environmental samples analyzed adipose tissue spiked with known amounts of dioxins, dibenzofurans, and common chemical interferences. Samples were extracted at a single laboratory (NIEHS) but analyzed by each participant using their own procedures. The findings clearly show that parts per million analyses are routinely possible using different analytical methods. Instrument operation criteria, analyst competency and reference standards were shown to be essential to accurately quantitating residue levels.

FUTURE DIRECTIONS: Emphasis will be placed on producing analytical reference standards (for routine trace analysis. Investigations to determine if biological tissues adipose tissue) contain a "fingerprint" distribution of dioxin residues are being considered as part of methods development research for organic compounds in biological tissues.

PROJECT III

TITLE: Quality Assurance Support

CONTACT: Ron Mitchum, EMSL, Las Vegas, Nevada

OBJECTIVES: Produce quality assurance reagents and a guidance document for sampling and analyzing 2,3,7,8-TCDD in air, water, soil/sediment, and fish.

BACKGROUND/RATIONALE: To provide quality assurance oversight to the Agency's "Dioxin Strategy". This role includes providing quality assurance guidance, standard reference materials and viable methods for analysis.

CURRENT STATUS: An interim quality assurance document was produced in FY'84. It was used by the Office of Water to produce specific guidance for the regions to collect samples for the "National Dioxin Study". This document was also used by the Troika and the Contract Laboratory Program to develop analytical methods to analyze samples in the "National Dioxin Study". A final document was produced in April, 1985.

EMSL-LV assayed these reference isomers for purity and distributed them into ampules. Reference standards have been sent to ECL, Bay St. Louis for use in the Troika. Additionally, EMSL-LV will use these reference standards to produce quality assurance samples for the contract laboratory program. EMSL-LV will use these samples to qualify contract laboratories which will replace the Troika in conducting routine 2,3,7,8-TCDD analysis to support the Dioxin Strategy.

EMSL-LV has established an interagency agreement with the Centers for Disease Control to produce key reference isomer standards for the higher homologues of dioxin and for dibenzofurans. A standard procedure for purity assays will be developed and methods validation exercises will be conducted to determine the ability of existing methods to distinguish among related isomers and common interferences frequently encountered in trace environmental analyses.

EMSL-LV is providing the HWERL-Cincinnati with the following quality assurance support for the mobile incinerator field demonstration of incineration of soil and wastes contaminated with 2,3,7,8-TCDD in Missouri. The laboratory is providing reviews of: (1) contractor procedures for collecting and analyzing combustion samples from the incinerator; (2) contractor quality assurance plan; and (3) sampling and analytical procedures used in permit application.

EMSL-LV is auditing activities at the incinerator and the laboratory to ensure that these procedures are being carried out properly. EMSL-LV will standardize these procedures and produce guidance documents which can be used to support future incineration operations. Furthermore, EMSL-LV will produce quality assurance samples which can be used to qualify other contract laboratories to conduct these kinds of analyses.

FUTURE DIRECTIONS: EMSL-LV will produce and distribute quality assurance reagents for trace analyses in the Contract Laboratory Program as part of the special analytical services.

PROJECT IV

TITLE: GC/MS Methods Development for CDD's and CDF's

CONTACT: William L. Budde, EMSL, Cincinnati, Ohio

OBJECTIVES: Produce a high resolution gas chromatography/low or high resolution mass spectrometry method for total chlorinated dibenzodioxins (CDDs) and total chlorinated dibenzofurans (CDFs) by level of chlorination. Provide options in the method for isomer specific analyses or penta-, hexa-, hepta-, and octachlorodibenzodioxins and dibenzofurans. Automate these methods to provide cost-effective analyses by development of appropriate software. Develop appropriate quality control techniques including tests for dynamic mass spectrometer and chromatography resolution under the exact conditions used for the analyses.

CURRENT STATUS: Work is being conducted at Battelle-Columbus Laboratories under contract. Full mass range mass spectra were acquired for 20 CDD and CDF congeners. A computer data library was built and verified for correctness. Initial testing of an automated identification procedure was begun. Efforts are being made to acquire additional standards through an exchange with another agency that has an intensive synthesis program underway.

FUTURE DIRECTIONS: This program will be continued during FY'86 with the goal of evaluating the automated method in a multi-laboratory field test during the second half of the year. Samples will be obtained from RCRA type wastes including wood preservative plant wastes and incinerator residues.

ENVIRONMENTAL EFFECTS RESEARCH

Environmental effects research is designed to address the issues of rate movement, toxicity and effects of dioxins in the environment. This effort will provide critical information in defining food chain contamination and human hazard associated with dioxin contaminated wastes. The research consists of projects on: (1) Study of the adsorption/desorption of 2,3,7,8-TCDD in soils; (2) Investigation of uptake and bioaccumulation of 2,3,7,8-TCDD of fish; (3) Determination of the uptake by plants, (4) Evaluation of uptake of 2,3,7,8-TCDD in large animals; and (5) A study of comparative bioavailability of 2,3,7,8-TCDD from New Jersey and Missouri soils in laboratory animals.

In addition, a study of photodegradation of 2,3,7,8-TCDD on soil surfaces will be initiated during FY'86. Descriptions of each project are given below.

PROJECT I

TITLE: Fate of Dioxins: Potential for 2,3,7,8-TCDD Transport in Soils Using Both Static and Dynamic Systems

CONTACT: Carl Enfield, RSKERL, Ada, Oklahoma

OBJECTIVES: To evaluate the adsorption, desorption and mobility of 2,3,7,8-TCDD in soils.

BACKGROUND/RATIONALE: To predict the rate of movement and transformation of 2,3,7,8-tetrachlorodibenzo-p-dioxin in soil and ground water in the presence and absence of codisposed organic solvents. These data are necessary to assess the potential for human exposure to dioxins and to make rational decisions regarding the removal and disposal of dioxin-contaminated soils. These data will also aid in the development of technologies to desorb dioxin from soils and to detoxify or destroy dioxins in contaminated soils. Saturated and unsaturated zone microcosms with soils from control sites near contaminated dioxin sites will be used to determine rates of movement and transformation of 2,3,7,8-tetrachlorodibenzo-p-dioxin both by dosing the columns with radio-labeled compound and also by measuring the aged dioxin released from the contaminated soils column, if any.

CURRENT STATUS: Work currently underway is evaluating the kinetic and equilibrium characteristics of sorption and desorption of 2,3,7,8-TCDD between soil and water and cosolvent mixtures of water with toluene and methanol. Six soils, ranging in organic matter content from 0.9 to 6.3% are being investigated. For liquid phases involving mixtures of water and methanol, isotherms generally exhibit linear behavior for soils with organic matter greater than 1%, while isotherms for soils with lower organic matter content were nonlinear. For isotherms involving toluene and methanol, sorption coefficients were generally low (ten or less).

Sorption of 2,3,7,8-TCDD to soils from water/methanol, methanol and toluene liquid phases has been investigated by batch isotherm testing. Soils used in these experiments ranged in fraction organic content from 0.0062 to 0.0765. Equilibration times of 1, 3, 10, 30, and 90 days were employed, with consecutive desorption points determined from soils previously equilibrated for 1 and 90 days in sorption. Maximum observed partition coefficient K_D 's for water/methanol varied from 160 to 1490 mL/g. These K_D 's appear to increase significantly with time in a manner which was roughly related to f_{OC} ; the low- f_{OC} soil showed little increase in K_D with time, while sorption increased by about a factor of five for the high- f_{OC} soil. Intermediate- f_{OC} soils (f_{OC} ranging from 0.0097 to 0.0344) exhibited a sorption maximum at about 10 days, with an apparent lower capacity at longer equilibration times (90 days). Sluffing of organic materials from the soils, swelling of clays, and/or diffusion limitations may explain these observations.

Similar behavior is apparent for toluene and methanol as liquid phases. However, because K values in these liquids are so low (on the order of one or less) these could not be evaluated thoroughly. These results have important implications on modeling TCDD transport in soils in the presence of cosolvents, since the typical assumptions of rapid equilibrium and linear sorption isotherms may not be valid.

FUTURE DIRECTIONS: Degradation of 2,3,7,8-TCDD and other isomers in soils mediated by photodegradation and biotic means will be investigated.

PROJECT II

TITLE: Sorption/Desorption of 2,3,7,8-TCDD in Contaminated Soils

CONTACT: Michael Roulier, HWERL-Cincinnati, Ohio

BACKGROUND/RATIONALE: The environmental persistence and toxicity of 2,3,7,8-TCDD created an acute awareness of the need to clean up identified dioxin sites. Many investigators have documented the extreme immobility of TCDD in soils; however, there have been no reported investigations dealing with the potential mobility of TCDD in native contaminated soils. Soil samples collected for this investigation were taken from an abandoned 2,4,5-T manufacturing facility and a scrap metal yard in New Jersey, and from horse arenas, roadways, and residential property in Missouri. These samples were historically contaminated with either chemical residues or waste oils containing TCDD.

OBJECTIVES: Partition coefficients (K_p) for 2,3,7,8-TCDD in soils and correlative soil physicochemical parameters were determined. Consistency of a K_{oc} value derived from soils was used to obtain a predicted value.

CURRENT STATUS: The K_p ranged from 0.3 - 1.3×10^7 ml/g with a mean of 1.8×10^6 ml/g. These values seem realistic compared to previous work suggesting that the K_p would be in the range of 1 - 10×10^7 ml/g. Mean log K_{oc} for the two batch methods and the intact cores were 7.39, 7.58, and 7.55; these values were within one standard deviation of a value of 6.95 predicted with data from previous studies.

TCDD was found to be more soluble in soils containing higher amounts of halogenated, semi-volatile compounds. Organic contaminants in wastes other than TCDD may be more significant than soil properties in controlling solubility and movement of TCDD in soil, once the adsorptive capacity of the natural organic components (i.e., humic acids) has been exhausted. The solute transport model used and the data collected during the study led to the determination that 2,3,7,8-TCDD would be essentially immobile in water percolating through the soils studied. Other transport mechanisms, such as wind and water erosion, are likely to be far more significant.

FUTURE DIRECTIONS: A proposal for additional cooperative research has been made to the U.S. Air Force. Of particular interest are locations where large amounts of solvents or low solubility organic compounds such as chlorinated benzenes and higher molecular weight materials were added to soil in the waste containing TCDD or at some later time. The tendency to employ clean, native soils spiked with TCDD should be avoided.

REFERENCES:

Jackson, D.R., et al. "Leaching Potential of 2,3,7,8-TCDD in Contaminated Soils." Proceedings of the EPA HWERL 11th Annual Research Symposium, Cincinnati, OH, Apr 29-May 1, 1985. EPA/600/9-85/013, pp. 153-168 (1985).

Ford, J.J., Hirwe, A.S. and Frawley, J.P. "The Influence of Toluene on the Leachability of TCDD Fran Soil," Hercules, Incorporated, Wilmington, DE, 19 August 1983.

Moreale, A. and Van Bladel, R. "Adsorption and Migration of Lindane (1,2,3,4,5,6-Hexachlorocyclohexane) in Soil." Parasitica, 34(4), 233-255 (1978).

Senesi, N., Testimi, C. and Mette, D. "Binding of Chlorophenoxy Alkanoic Herbicides from Aqueous Solution by Soil Humic Acid." Environmental Contamination. International Conference sponsored by the UN Environmental Programme, Imperial College, London, U.K., pp. 96-101 (1984).

"Times Beach Soil Core Analyses." Memorandum of May 25, 1983 from J.D. Wilson, State of Missouri Department of Natural Resources, to G. Roush, M.D.

Jackson, D.R., Roulrier, M.H., Grotta, H.M., Rust, S.W. and Warner, J.S. "Solubility of 2,3,7,8-TCDD in Contaminated Soils." In: Symposium on Chlorinated Dioxins and Dibenzofurans in the Total Environment, III. C. Rappe, G. Choudhary and L.H. Keith, eds. Proceedings of the ACS Division of Environmental Chemistry at the 189th National Meeting, April 28 - May 3, 1985, Miami Beach, FL. (1985).

PROJECT III

TITLE: Uptake, Bioaccumulation and Depuration of Dioxins by Fish

CONTACT: Philip Cook, ERL-Duluth, Minnesota

OBJECTIVES: To evaluate the uptake and bioaccumulation of 2,3,7,8-TCDD by fish from municipal incinerator fly ash samples, contaminated sediments, and water.

BACKGROUND/RATIONALE: There is a need to determine the potential for uptake of dioxins by plants, fish and large animals. The uptake data will be used in defining the potential biomagnification of dioxins in food chain systems. Recent findings of the existence of dioxins at trace levels in various compartments of the environmental media pose a great concern over human exposure. It is critical to know the bioavailability of dioxins to ecosystem species comprising the food chain system. Information on the biomagnification of dioxins in food webs will be used in estimating human and ecosystem risk due to dioxins. The rate of uptake of 2,3,7,8-TCDD by fish will be determined by analysis of organism tissues after controlled exposure to contaminated water or sediments. The biomagnification and bioaccumulation factors for 2,3,7,8-TCDD and other TCDD and TCDF isomers will be calculated.

CURRENT STATUS: Work on the selective accumulation in fish of 2,3,7,8-TCDD from two municipal fly ash samples has been **completed** and a manuscript has been published in "Chemosphere". This work is now being extended to study other dioxin and dibenzofuran isomers.

A 60 day **flow-through** exposure of fathead minnows and carp to **1,2,3,4-TCDD** has just been completed. Exposures of fish to a mixture of 1,2,3,4; **1,3,6,8** and **1,3,7,9-TCDD** are in progress. Exposure of fathead minnows and carp to 2,3,7,8-TCDD and will begin in August 1985. Rainbow trout are being exposed to 2,3,7,8-TCDD and **2,3,7,8-TCDF** at **Battelle-Columbus** Laboratories through funding provided by **ERL-Duluth** to the U. S. Fish and Wildlife Service Columbia, Missouri **laboratory**. True **bioconcentration factors** are expected to exceed **30,000** for fish.

The Petenwell Reservoir on the Wisconsin River is being used as a field site to study dioxin bioavailability from sediments. Carp in the reservoir contain approximately 70 ppt of 2,3,7,8-TCDD and the sediments in the range of **30-to-200** ppt. Young carp were exposed to sediment from Petenwell containing 40 ppt 2,3,7,8-TCDD in a 55 day **flowthrough** exposure. **Fish** were sampled periodically throughout the exposure and the remaining **fish** will be analyzed during a **60-day** depuration phase. After 55 days the fish contained 8 ppt 2,3,7,8-TCDD.

FUTURE DIRECTIONS: Bioaccumulation studies will be extended to determine the **bioaccumulation** factors of TCDD and TCDF from contaminated sediments.

REFERENCE;

Kuehl, Douglas W., Cook, Philip M., Batterman, Lothenbach, Douglas, "Bioavailability of 2,3,7,8-TCDD From Municipal Incinerator Fly Ash to Freshwater Fish." **Chemosphere** 14, 427-437 (1985).

PROJECT IV

TITLE; Uptake of **Dioxins** by Plants

CONTACTS: Harold Kibby, **ERL-Corvallis**, Oregon

OBJECTIVES: Evaluate the uptake of dioxins by **plants**

Identify plant species capable of uptake of dioxins and can be used in decontaminating waste sites.

Investigate how plants function in relationship to the movement or **dioxins** in the natural and agricultural environments.

BACKGROUND/RATIONALE: The plant uptake data are critical in **defining** the potential **biomagnification** of dioxins in food chain systems. Recent findings of the existence of dioxins at trace levels in various compartments of the environmental media pose a great concern over human exposure. It is critical to know the bioavailability of dioxins to ecosystem species comprising **food chain** system.

Information on the **biomagnification** of dioxins in food webs will be used in estimating human and ecosystem risk due to dioxins. Plant uptake data will also be used in developing plants as a probe for detoxifying dioxin-contaminated soils. The rate of uptake of 2,3,7,8-TCDD by plant will be determined by tissue or organism analysis after controlled exposure of contaminated water or soil. The **biomagnification** factors for 2,3,7,8-TCDD will be calculated. This work is at its initial stages.

CURRENT STATUS: A literature view on plant uptake and metabolism of dioxins has been **completed**. The draft report is available for internal use. Through a cooperative agreement with Oregon State University, work has begun to **develop** a model for plant uptake of dioxins. The model will be based on critical pathways related to chemical movement via **xylem**. This model will be **extended** to test selected dioxins.

FUTURE DIRECTIONS: **Comparative** plant uptake and kinetics of several chlorinated dioxin **isomers** will be evaluated,

PROJECT V

TITLE: Uptake of Dioxins by Large Animals.

CONTACT: Harold Kibby, ERL-Corvallis, Oregon

OBJECTIVES: To evaluate the uptake of 2,3,7,8-TCDD from contaminated soils **by** dairy cows.

To evaluate the food chain contamination to human via animal products.

BACKGROUND/RATIONALE: The animal uptake data are critical in defining the potential **biomagnification** of dioxins in food chain systems.

Information on the **biomagnification** of dioxins in food webs will be used in estimating human and ecosystem risk due to dioxins. The rate of uptake of 2,3,7,8-TCDD by large animals will be determined by tissue or organism analysis after controlled exposure to contaminated soil. The uptake of 2,3,7,8-TCDD will be calculated.

CURRENT STATUS: The investigation is being carried out through two cooperative agreements. The University of California at Davis is determining if sheep or goats may be used as surrogates for dairy cows. Examination of the metabolic activity of isolated liver **hepatocytes** and rumen microorganisms on 2,3,7,8-TCDD is being used as a probe. Early effort on this project were directed towards making necessary laboratory setups to handle dioxins. **Work** on establishing **cytotoxicity** of TCDD to isolated hepatocytes from three species. The project was added to ongoing studies.

The second cooperative agreement with Texas A & M University will be directed toward determining the actual uptake, metabolism, distribution, and elimination of TCDD via milk and wastes in dairy cow. The results will be compared with existing data.

FUTURE DIRECTIONS: After completion of this study, an evaluation will be made for future work on uptake of other isomers by large animals.

PROJECT VI

TITLE: Bioavailability of 2,3,7,8-TCDD from Contaminated Soils in Laboratory Animals.

CONTACT: Rizwanul Haque, EPA Headquarters, Washington, D. C.

OBJECTIVES: To compare the bioavailability of 2,3,7,8-TCDD in laboratory animals from contaminated soils from wastes sites in Missouri and New Jersey. Evaluate the bioavailability data in terms of human health significance.

BACKGROUND/RATIONALE: The occurrence of dioxins and other chemicals in hazardous waste sites has been demonstrated by many studies. A critical evaluation of the human health hazard associated with such contamination is important.

Recent studies of McConnell and co-workers have shown that 2,3,7,8-TCDD was readily bioavailable to laboratory animals when such animals were exposed to Times Beach, Missouri contaminated soils. A preliminary investigation with New Jersey contaminated soil showed negligible bioavailability to laboratory animals. These two findings suggest that a comprehensive investigation of the factors affecting bioavailability is required to fully evaluate the health risks associated with contaminated wastes.

CURRENT STATUS: The acute toxicity to guinea pigs of TCDD-contaminated soils from Newark, New Jersey, and Times Beach, Missouri have been measured. Guinea pigs were dosed by gavage with single doses of 1,3, and 10 ug TCDD equivalent/kg animal (with appropriate controls) and observed for sixty days. After the first death due to TCDD was observed, two animals from every group were killed, autopsied, and tissue samples taken for analysis. Guinea pigs were observed for toxic signs and time of death, and survivors were sacrificed 60 days after dosing.

Growth curves of all surviving animals were comparable except for Times Beach soil at 3 ug/kg TCDD equivalent, which had reduced growth for about one half of the survivors. At 10 ug/kg TCDD equivalent Times Beach soil, the few surviving guinea pigs grew at rates comparable to clean soil treated animals.

Cause of death was determined by **autopsy**, and included **TCDD syndrome**, bacterial **pneumonia**, TCDD syndrome with slightly affected **pneumonial** lungs, and assorted other causes not related to TCDD that generally affected one animal per group. In a few cases, cause of death could not be unequivocally determined. Randomly selected **animals** were sacrificed at seven **days**, and all surviving animals were sacrificed sixty days after dosing for tissue analysis.

These results show that the guinea pigs were highly susceptible to TCDD added to soil and to the Times Beach soil at 10 **ug** TCDD equivalent/kg body weight. The estimated **LD₅₀** was approximately 8 ug/kg, Newark soil at similar TCDD equivalent concentration was not nearly as toxic.

These results also show that in laboratory animals the **Times Beach** soil is considerably more toxic than the Newark soil, to laboratory animals and the bioavailability of TCDD from the Times **Beach** soil is much greater. These results confirm the the early conclusions reached by **McConnell et al.** (1984).

FUTURE DIRECTIONS: Bioavailability studies will be continued with emphasis on a better understanding of the role of soil **parameters** as well as mechanistic **factors**.

REFERENCES;

McConnell, E. E., Lucier, G. W., Rumbaugh, R. C., Albro, P. W., Harvan, D. J. Hass, J. R., Harris, M. W. "**Dioxin** in Soil; Bioavailability After **Ingestion** by Rats and Guinea Pigs." Science Vol. 223, p. 1077 (March 1984).

Umbreit, T. H., **Patel**, D., and **Gallo**, M. A. Acute Toxicity of TCDD Contaminated Soil **from** An Industrial Site. Chemosphere, in press.

HEALTH ASSESSMENT RESEARCH

The objectives of the health assessment research program are to develop exposure and risk assessment methodologies for dioxins and related compounds, to provide documents for Agency use in evaluating risks associated with dioxin exposure, and to contribute to the necessary data base for better evaluating human health and the risks associated with exposure to dioxins. The common theme of the health assessment program is to provide the means to better assess the risks associated with human exposure to dioxins.

The major projects included the development of a document describing the hazard assessment methods used by EPA, CDC and FDA in assessing risks for dioxin, the development of human exposure assessment methods for dioxin-contaminated soils, and an analysis of the pharmacokinetics of TCDD in monkeys. In FY'84, a collaboration study was also undertaken with NIOSH to establish a dioxin registry for potentially exposed U. S. production workers.

Interest in developing alternative rapid analytical procedures for 2,3,7,8-TCDD analysis, led to research to produce a monoclonal antibody to 2,3,7,8-TCDD that would have possible application in screening tests. Mice were immunized with 2,3,7,8-TCDD and hybridomas produced. Clones have been recovered and are being characterized. If characterization is satisfactory and the antibody is of sufficiently high titer, efforts will be initiated to determine if monoclonal antibodies can be used in exposure assays.

Short-term in vitro bioassays and chemical analytical techniques for especially synthesized higher chlorinated CDFs and CDDs are being developed for comparison to in vivo animal assays. These in vitro assays will be evaluated with regard to their usefulness in providing complementary information or in serving as surrogates for in vivo toxicity assays, including antagonistic or synergistic interactive effects. Descriptions of health assessment projects follow:

PROJECT I

TITLE; Risk Assessment Approach for 2,3,7,8-TCDD.

CONTACT: Charles Ris, EPA Headquarters, Washington, U. C.

OBJECTIVE; The objective of this project was to assemble and discuss in one document the risk assessment methods for 2,3,7,8-TCDD used by EPA, and to contrast and compare EPA's methods to the approaches which have been adopted by CDC and FDA. A second document will inventory and compare methods used by other nations and states.

BACKGROUND/RATIONALE: The risk assessment methods used by three principal Federal agencies are known to vary enough that estimates of risk differ by two or three orders of magnitude. The variables responsible include preferences in procedures used to extrapolate from high to low doses in the analysis of animal data, the use of body weight or body surface area in the extrapolation of animal data to humans, and assumptions such as the number of grams of fish eaten and amount of soil ingested by children.

Originally it was hoped that a consensus could be reached with CDC and FDA on methods, procedures, preferences, and **assumptions** that would be used to assess the risks for 2,3,7,8-TCDD. Ultimately it was decided that obtaining a consensus was not possible because of the differing regulatory mandates, and emphases of the **three** agencies.

CURRENT STATUS: The initial 2,3,7,8-TCDD document has been completed and is available as an EPA report through the National Technical Information Service (**NTIS**). This document was compiled by three OHEA staff from existing documentation from EPA, CDC, and FDA. The supplementary inventory of other assessments is being initiated during the summer of 1985 and should be completed in October/November 1985.

FUTURE DIRECTIONS: It is projected that work beyond **FY'85** will shift to updating the information contained in the various **recently completed** health assessment documents, particularly with regard to the designation of new scientific information (such as in the areas of bioavailability, **pharmacokinetics**, **immunotoxicity**, developmental disorders, body burden, and epidemiology) which may be useful in reducing the degree of uncertainty in risk assessments for dioxins. In addition, a conference is planned which will convene scientists involved in work relating to dioxin body burden, particularly with regard to concern over recent report on dioxin residues in human adipose tissue and in nursing mother's milk.

REFERENCES: U.S. EPA. 1985. "Health Risk **Assessment** Approach for **2,3,7,8-Tetrachlorodibenzo-p-dioxin.**" Compiled by Mukerjee, D., Ris, C. H. and Schaum, J. EPA-600/8-85-013.

PROJECT II

TITLE: Exposure Assessment Methods for **2,3,7,8-TCDD**

CONTACT: John Schaum, EPA Headquarters, Washington, D. C.

OBJECTIVE: The objective of this project, based on the original charge, was to develop relevant, likely scenarios through which humans could be **exposed** to **2,3,7,8-TCDD** spilled on or contaminating soil and to **develop** monographs for approximating upper bound carcinogenic risk for persons exposed via the scenarios which **were** developed. A more recent objective has been to extend exposure assessment methods to include chemical **specific-factors** for dioxins other than 2,3,7,8-TCDD.

BACKGROUND/RATIONALE: Under EPA's Dioxin Strategy, ORD was charged with the responsibility of establishing exposure scenarios to be used in estimating dioxin exposure under conditions likely to be encountered by man in the environment; in addition, nomographs **were** to be developed for converting from dioxin contamination levels in the environment to upper risk limits for the exposure scenarios that **were** established.

CURRENT STATUS: Methods and documents were prepared mostly through in-house efforts in FY'84, and will be prepared mostly through contractor efforts in FY'85 and beyond. Several reports have been developed and are available. In the first, five pathways were chosen for analysis in developing exposure scenarios and nomographs. These were: dust inhalation, fish ingestion, dermal absorption, soil ingestion, and beef and dairy product ingestion. The first report nomograph describes methods to use minimal data and the nomographs developed for the five principal pathways to provide a quick approximation of upper bound risk.

A second report describes a more sophisticated approach in estimating risk; these methods require more input data and allow for the use of temporal variation for some parameters and for the use of ranges of values, thus providing a more realistic estimate of risk. A third report provides guidance of conversion factors required in the use of nomographs to estimate risk. This work is being extended in FY'85 to provide methods for including chemical-specific factors (such as absorption, bioconcentration, plant uptake, and degradation properties) for other dioxin and dibenzofuran congeners.

FUTURE DIRECTIONS; Dioxin exposure assessment work beyond FY'85 will center on refining methods to include new scientific advances and to fill data gaps which have been identified in the scientific data base. These may include factors such as atmospheric photolysis rates, estimation or determination of other needed physical-chemical properties, estimation of dermal absorption through determination of amounts of soil which accumulate on skin, etc.

REFERENCES:

Schaum, J. 1984. Interim Report on Risk Analyses of TCDD Contaminated Soil. Exposure Assessment Group, Interim Report (3/5/84).

Schaum, J. 1984. "Risk Analysis of TCDD Contaminated Soil," EPA-600/8-84-031. Exposure Assessment Group, NTIS No. PB 85 146704/AS (November 1984).

U.S. EPA. "Dioxin Transport from Contaminated Sites to Exposure Locations: A Methodology for Calculating Conversion Factors." Prepared by Dawson, G.W., Meuser, J.M., Lilga, M.C. EPA/600-8-85-012. NTIS No. PB 85 214310 (1985).

PROJECT III

TITLE; Pharmacokinetics of 2,3,7,8-TCDD in Monkeys

CONTACT: Peter Voytek, EPA Headquarters, Washington, D. C.

OBJECTIVES: To investigate the distribution and rate of transport of 2,3,7,8-TCDD in Rhesus monkeys; to evaluate the effect of 2,3,7,8-TCDD diet on birth weight

and other **breeding** characteristics in Rhesus monkeys; to determine the effect of **TCDD** on lymphocyte cells.

BACKGROUND/RATIONALE: Not enough is known about the behavior and fate of **2,3,7,8-TCDD** once it has entered the body. To help remedy this gap in our **understanding**, and **thus**, to facilitate a more accurate estimate of **risk** to man, **data** is being collected and analyzed from Rhesus monkeys which had been fed **2,3,7,8-TCDD** at the University of Wisconsin.

CURRENT STATUS: This project is being funded under a grant to the University of Wisconsin. The latest 6-month progress report on this project **outlines** the status of the work in four general **areas**:

- **Distribution of TCDD in Various Tissues:** Results show that bone marrow and axial lymph nodes have higher levels of TCDD than other tissues. The tissues of an animal that gave birth, and nursed and weaned an infant during the latter **stages** of exposure, **did** not have **detectable** levels of TCDD in her tissues. Tissues from a stillborn from a mother **exposed** to TCDD are being analyzed for the **compound** to determine tissue distribution in the offspring as **compared** to maternal levels.
- **Kinetic Studies:** Currently seven adipose tissue samples have been **obtained** at **3-month** intervals on **three** animals since the diet of TCDD **has** been terminated. The **half-life** determination **will** be completed using these data.
- **Breeding Studies of Animals 1 1/2 Years off Diets of 5-and-25 ppt TCDD:** There appears to be no effects of TCDD on numbers of live birth, birth weights and weaning **weights**, as **compared** to those **animals** that gave birth while on the diet. A study is in progress to **determine** TCDD levels in fat in mothers on the day of birth, their offspring at weaning, the **mothers** at weaning, and the amount of TCDD in the **mothers'** milk.
- **Lymphocyte Studies:** Thirty-five human monoclonal antibodies have been examined and six have **been** shown to have cross reactivity with Rhesus monkeys. Four animals exposed to 25 ppt TCDD have been examined with respect to lymphocyte stimulation by three **mitogens**. The results are too preliminary to draw any conclusions. An assay for detecting gene mutations in lymphocytes of animals exposed is in progress.

FUTURE DIRECTIONS: Health Assessment work beyond **FY'85** is projected to **include** an evaluation of behavioral teratology and **immunotoxicity** in offspring of Rhesus monkeys fed TCDD, and the development of **TCDD** antibodies in the blood of Rhesus monkeys. In addition, cytosol receptor binding and **AHH** induction bioassays will be **refined** for the detection of dioxin congeners **with high** bioactivity.

PROJECT IV

TITLE: Dioxin Registry

CONTACT: Jack Griffith, **HERL/RTP**.

OBJECTIVES: The registry data are being used to conduct a retrospective cohort mortality study.

BACKGROUND/RATIONALE: Lack of sufficient exposure information often is the reason that a causal relationship cannot be drawn between an agent and a human effect. This project will attempt to provide that exposure information for a population potentially heavily exposed.

CURRENT STATUS: Partial funding for a study being conducted by NIOSH. Funding for this study is distinct from that provided under the National Dioxin Study. As of September 30, 1984, thirteen sites have been included in the registry. About 6,000 workers have been identified, and standard methods of follow-up are being used to determine their vital status. Demographic data have been coded for all workers, and the coding of detailed work histories is in process. Discussions of the chemical process and job duties have been completed at nine sites and have been initiated for the remaining sites. Companies have been contacted to request all data containing analytic measurements of dioxin in products, wastes, and process streams. This information will be utilized in the construction of the exposure matrix for the study.

Besides an Office of Health Research contribution to begin the registry FY'84, Superfund resources are being provided to the register for a three-year period that began in FY'84.

FUTURE DIRECTIONS: Continuation of the project is expected with additional subpopulations to be used by the Centers for Disease Control to carry out additional "dioxin" epidemiology projects.

PROJECT V

TITLE: Monoclonal Antibody.

CONTACT: Michael Dellarco, EPA Headquarters, Washington, D. C.

OBJECTIVES: Produce a monoclonal antibody to 2,3,7,8-TCDD.

BACKGROUND/RATIONALE: Monoclonal antibody to 2,3,7,8-TCDD may be a useful tool in subsequent toxicology studies in laboratory animals and may be applied to evaluations of human exposure.

CURRENT STATUS: An interagency agreement has been established with Oak Ridge National Laboratory to produce a monoclonal antibody. Both Burroughs Welcome,

Inc. and Texas A & M University are providing the chemical synthesis support. Dr. Phil **Albro**, **NIEHS**, serves as a senior science advisor to the project.

Texas A & M produced **immunogens** which Oak Ridge used to evoke antibody production in laboratory mice. Antibodies were produced in **these** mice, **hybridomas** were made and 30 clones were recovered and stored in the **freezer** for characterization.

Six candidates were chosen for initial characterization by Oak Ridge. Both Texas A & M and Burroughs Wellcome attempted to produce the necessary reagents to characterize the resulting clones. **Radiolabelled** material recently has been sent to Oak Ridge by Texas A & M. Characterization studies are being conducted in **FY'85** at Oak Ridge to **determine** the specificity and avidity of candidate clones.

FUTURE DIRECTIONS: **EMSL-Cincinnati** has contracted with the Lawrence **Livermore** Laboratory to produce a monoclonal antibody assay to detect **2,3,7,8-TCDD** in soil matrices in the Innovative Technologies Research program. We have agreed to coordinate with Lawrence **Livermore** by sharing **immunogens** and other **reagents**. Lawrence **Livermore**, which uses a different strain of mice for producing hybridomas and an enzyme identification assay instead of a **radiolabelled** assay (which Oak Ridge is **developing**), will share their **reagents** with Oak Ridge. This will conserve resources and may help to resolve technical problems which may arise because two independent laboratories will be available to research **problems**.

PROJECT VI

TITLE: Short-Term Bioassays for **Polychlorinated Dibenzo-p-Dioxins (PCDDs)**

CONTACT: Richard Phillips, **HERL/RTP**, North Carolina

OBJECTIVES: Synthesize all higher chlorinated **PCDFs** and several **PCDDs**, test them individually and together in mixtures in **receptor-mediated in vitro** bioassays, and compare **in vitro** bioassay results for quantitative utility with parallel **in vivo** assessments.

BACKGROUND/RATIONALE: **PCDDs** and **PCDFs** are highly toxic chemicals which are found as by-products in several industrial chemical preparations and are formed as by-products in numerous combustion processes. **PCDDs** and **PCDFs** have been detected in diverse environmental samples including water, fish, wildlife and humans. In addition, there have been numerous human exposures to these chemicals; such as exposures during the Seveso, Italy, and Times Beach, Missouri, contamination incidents, **Yusho** poisoning in Japan and Taiwan (**PCBs + PCDFs**), and exposure to **PCDFs** as a result of **PCB** fires in places like **Binghamton**, New York.

Although the 2,3,7,8-substituted PCDDs and PCDFs are the most toxic members of both groups, there are several congeners within each series that are also highly toxic. Moreover, many exposures to these compounds usually involve mixtures and not single compounds. However, due to lack of analytical standards and toxicological information on individual PCDFs and PCDDs and their mixtures, rational environmental and human health impact assessments to these toxic chemicals have not been possible. This project proposes an integrated chemical-toxicologic approach which is planned to provide measures for rapid assessment of potential human risks and develop data which will provide a sound scientific underpinning for risk management decisions.

CURRENT STATUS: All of the higher chlorinated PCDFs and several PCDDs will be synthesized and their chemical and analytical properties thoroughly investigated. This will permit the isomer-specific analysis of PCDF mixtures, using a combination of analytical methodologies. It also will complement the currently available PCDD analytical methodologies.

Three receptor-mediated in vitro bioassays, including dioxin receptor binding, AHH/EROD enzyme induction in rat hepatoma H-4-II-E cells and XB cell keratinization, will be used to determine and compare the quantitative effects of diverse PCDD and PCDF compounds, PCDD and PCDF reconstituted mixtures and environmental extracts of PCDD and PCDFs in these assays. The utility of these in vitro bioassays as predictors of toxicity will be quantitatively assessed by comparing the ED in vitro bioassay data for individual PCDD and PCDFs and their mixtures with their in vivo ED 30-50 values for AHH/EROD induction, immunotoxicity, body weight loss, and thymic atrophy in immature male Wistar rats. Finally, a series of experiments with reconstituted mixtures of PCDDs and PCDFs will probe for possible synergistic, additive or antagonistic interactive effects. Since two recent papers report conflicting interactive effects (synergistic and antagonistic), it is critically important to resolve this issue.

FUTURE DIRECTIONS: Research will continue in Fiscal Year 1986.

REFERENCES:

Rizzardini, M., Romano, N., Tursi, F., Salmons, M., Vecchi, A., Sironi, M., Gizzi, F., Benfenati, E., Garattini, S., and Fanelli, R., Chemosphere, 12, 559 (1983).

McKinney, J. D., Choe, K., McConnell, E. E. and Birnbaum, L. S. Environ. Health Perspect., in press.

CHAPTER VII

FUTURE DIRECTIONS

The EPA Dioxin Strategy will be **modified** as Agency needs change and as the **state-of-the-art** in technology development moves forward. The development and evaluation of control technologies for destruction of dioxins will continue to be a very high **priority**. Health research will be expanded to develop improved techniques for estimating human health hazard, human exposure and assessing risks associated with **dioxin-contaminated** wastes. Monitoring, quality assurance and bioavailability research will also continue to be a high priority.

Greater emphasis will be given to coordinating the EPA **research** with other Federal agencies including CDC, **DOD, NIEHS**, and continued focus will be on information exchange at the international level through the newly established exchange program under **NATO/CCMS**. Research findings will be extended to **include** other dioxin **isomers** of chlorinated **dibenzodioxins** and **benzofurans**. If warranted, **bromo** dioxins will also be tested and appropriate experiments will be performed. The Agency will also consider some projects that include work on structure-activity relationships for dioxin **toxicity** prediction as suggested by the Environmental Defense Fund and National Wildlife Federation Petition. Specific research areas are described below,

TECHNOLOGY ASSESSMENT

The Agency will continue to evaluate and improve various technologies for cleaning up dioxin waste sites. **Work** on improving and field testing of the mobile incinerator system will **continue**. White rot fungus will be field tested in a small number of plots including at one of the contaminated horse arenas in Missouri: Work on in situ stabilization technique will also continue for the purpose of evaluating the leaching potential of dioxins.

The concept of using abandoned mines for **dioxin-contaminated** waste storage will be further tested including the feasibility of developing new mines for this **purpose**.

A comprehensive study will be conducted to understand the combustion process involved in the function of dioxins. This may include the following projects: (1) Determining the effects of feed precursors and gross elemental **composition** on formation of dioxins in combustion; (2) Studying the partitioning of CDDs and CDFs between the vapor and condensed phases; (3) Characterizing fly ash and **bioavailability**; and (4) Developing advanced **combustion** process monitoring techniques.

Modification of the APEG process, including **in situ RF** heating and on-site **slurrying**, will be evaluated with special emphasis on dioxin destruction, by product evaluation, and cost.

MONITORING

Research on human exposure **monitoring** including adipose tissue, blood and human milk analysis will **continue**. Standards for routine trace analysis will be produced and the priority of adipose tissue analysis will be considered. Research on the production of quality assurance reagents for trace analysis will also be produced for distribution. Screening methods to chemically characterize a group of **compounds** will be developed and validated from bioassays for screening.

ENVIRONMENTAL EFFECTS

In the area of environmental **effects**, continued emphasis will be placed on evaluating the bioavailability of dioxins in laboratory animals. Uptake of **dioxins** by plants and large animals will also be **evaluated**. The fate of toxicity of dioxins including transport, movement, leaching and degradation (biodegradation and photodegradation) will also be investigated. Effects of naturally occurring surfactants on dioxin water solubility and transport in surface and ground water will be determined, and intermedia material and transport model will be developed.

HEALTH ASSESSMENT

Health **effects** research will be accelerated. **Low-cost**, short-term bioassays measuring health effects of mixtures containing **CDDs** and **CDFs** will be developed. Tissue assay data will be evaluated for defining indications of exposure and correlating exposure to sources and control of these toxic agents. Mechanisms of toxicity will be studied as well as CDDs and CDFs, including structure/activity correlations. This will provide a reliable computational **procedure**, based on molecular reactivities, for assessing the toxicity of various substituted **dibenzo-p-** dioxins and **dibenzofurans**. Continued effort will be directed towards improving health risk assessment documents. Exposure models will be developed. Health assessment research using primates (Rhesus monkeys and marmosets) will continue with emphasis on general and behavioral teratology and **immunotoxicity** in offspring.