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WORKING SEMINAR

EFFECTS OF DIOXINS ON NATURE AND SOCIETY THE EXPERIENCE IN THE U.S.A.

26 Settembre 1985 - Aula Scarpa

PROGRAM

- ore 14.30 S.P. RATTI: Universita' di Pavia
 Opening talk "Effects of Dioxins on nature and Society"
- ore 14.45 B.J. FISCHMANN: V.A. Washington D.C.
 "Chloracne and the Agent Orange Problem in the USA"
- ore 15.15 A.F. YANDERS: University of Missouri, Columbia-Mo
 "Dioxin in Missouri"
- ore 15.45 D.G.BARNES, P.ROBERTS: E.P.A., Washington-D.C.
 "E.P.A. Risk Assessment of Chlorinated Dibenzo-pDioxine and Dibenzofurans (CCDs/CDFs)"
- ore 16.45 Coffee break
- ore 16.45 T.L. STODDART: Tyndall USAF Base-Florida
 "Demonstration of Innovative Remedial Action Technologies at United States Military Dioxin Contaminated Sites"
- ore 17.15 R.J. SCHREIBER: DNR Jefferson City-Mo
 "Times Beach Dioxin Research Facility"
- ore 17.45 D.G. BARNES: E.P.A., Washington-D.C.

 "Recent International Cooperation in Exchange of Information on Dioxins"

Sergio P. Ratti

Dipartimento di Fisica Nucleare e Teorica della Universita' Istituto Nazionale di Fisica Nucleare - Sezione di Pavia via A.Bassi, 6 I27100 Pavia (PV)

EFFECTS OF DIOXINS ON NATURE AND SOCIETY OPENING TALK

WHAT? 10000 LIRE A CUP OF COFFEE?



CONTEMORI da "La Repubblica" del 25 settembre 1985 $\label{eq:fig.1} \text{fig.1}$

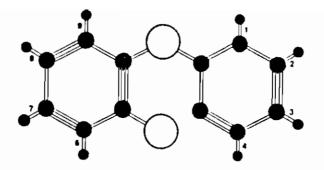


Fig. 2 - Molecular Structure of DiBenzo P-Dioxin

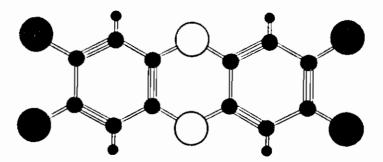


Fig. 3 - Molecular Structure of Tetra Chloro DiBenzo P-Dioxin

Taking advantage of the International Symposium on Dioxins and Chlorinated Compounds [DIOXIN 85] held in Bayreuth (Federal Republic of Germany) last week, some of us thought about the unique opportunity to have here in Pavia some among the most distinguished american scientists telling us about their experience on dioxin.

The Lombardy Region and the community of northern Italy experienced the Seveso episode. All of us heard about this specific case on the radio and the TV, but very few of us are aware of the fact that dioxin is not at all an "italian privilege".

The situation sketched in fig.1 [taken from the daily newspaper "La Repubblica"] needs at least a translation into english for the benefit of our distinguished guests.

We shall have, by all means, plenty of time in the future to eventually organize an "ad hoc" seminar on the italian dioxin case. However, this is the one and only chance we have our collegues coming from the other side of the Atlantic Ocean, as guests of our University.

I mean :

- Ms. A. Betty Fischmann, Chief Dermatologist, Chairperson of the U.S.A. Chloracne Task Force, in Washington, D.C., who had to take care of the unpleasant consequences of the use of Agent Orange to the soldiers and the veterans returning from the Vietnam war:
- Liutenent-Kernel Dr. Robert F. Olfenbuttel; Captain Jimmy

Corvette; Captain Terry L. Stoddart of the Environmental Research Complex of Tyndall Air Force Base in Panama City - Florida, who had to be concerned with the unpleasant job of taking care af the disposals of the "Agent Orange left over", when its use as an herbicide was forbidden;

- Dr. Donald G. Barnes, science advisor to the administrator of the Environmental Protection Agency [E.P.A.] in Washington D.C.; co-responsible for the several decisions made by the governmental authorities in the field of Environmental Protection;
- Dr. Robert J. Schreiber, former Director of the Division of Environmental Quality a, the Department of Natural Resources of the State of Missouri, who led the project of converting the accident at Times Beach, Missouri into an active Research Center, dedicated to the improvement of our knowledge on Dioxin;
- Prof. Armon F. Yanders, last but not least: the distinguished colleague of the University of Missouri at Columbia, who directs the very active and qualified Environmental Trace Substances Research Center and who played an important role in directing on scientific ground the action of the State of Missouri in the case of the Times Beach accident.

Dioxin is a magic word. Not one human death has been reported as "definitely" attributed [by the health authority] to it, in spite of the several "accidents" in which dioxins were involved (Love Canal in upper New York State; Times Beach in the State of Missouri; The Agent Orange during the Vietnam War; the Chemi-

cal Industries in West Germany, in West Virginia, in Seveso; the several municipal incenerators in the Netherlands, in Switzerland, Canada and Japan).

Table I, elaborated by the American Medical Association, collects a series of known industrial accidents in which human beings have been exposed to dioxins, summarizing the effects directly observed. Although there were deaths, the statistical evidence is questionable [but, just because the evidence is statistically questionable, I would not be personally surprised if some surprising long term effect would show up, even in Seveso].

Dioxin is a magic word and it evokes a variety of emotional reactions. The general public is worrying about the public health (the American Broadcasting Company - ABC - has even telecasted a movie by the Title "Mrs. Gibbs of Love Canal", to tell the degree of public emotion around dioxin). Toxicologists know of the severe effects on animals, but are uncertain about comparable consequences on human beings [perhaps soft tissue sarcomas?]. Regulators are worring because they must make decisions without having scientific certainties.

Dioxin is also used as the uncorrect abbreviation of Tetra-Chloro-Dibenzo-p-Dioxin, a chlorinated dioxin compound called more correctly TCDD.

The structure of dioxin is sketched in fig. 2. The dibenzop-dioxin consists of 2 benzene aromatic rings linked by two oxigen atoms. From one to eight chlorine atoms can take the place of an hydrogen atom, attached to the carbon atoms [their positions are numbered in fig. 2] usually available in the aromatic chains, to form any of the 75 possible chlorinated dioxins. In fig. 3 the TCDD proper [TetraChloro=four chlorine atoms; Dibenzo=two benzene rings] is sketched.

At present, due to the anomalous circumstances quoted above and, at least partially, induced by the general emotional interest, dioxin has been studied so exstensively that, in spite of the still numerous obscure aspects [the very late manifestation of epidemiological effects; the oncological and carcinogen manifestations, for instance] is becoming one of the best known toxics. Its migration in soil has been scientifically investigated; effects on guinea pigs, rabbits, monkeys, dogs, frogs have been studied. Even effects on some 60 volunteers are known.

Therefore, the learning of the U.S.A. experience on dioxins seems to be a very valuable contribution to the knowledge we need to put together. Not only for the so called experts but also for the student community of our University. It is an interdisciplinary subject which includes, among others, chemistry, genetic consequences, statistical evaluations.

The present Working Seminar has been organized jointly by the following Institutions as an interdisciplinary venture:

Dottorato di Ricerca in Fisica;

Dottorato di Ricerca in Scienze Genetiche (Genetica e Biologia

Molecolare);

Scuola di Specializzazione in Statistica Medica; Societa' di Merceologia (Delegazione Lombarda); Istituto Ricerche Sicurezza Industriale.

Therefore, while I have the privilege of opening the working session, I wish to thank the collaboration of prof. Alessandra Marinoni, prof. Luigi De Carli and prof. Vincenzo Riganti who, all together, made this Seminar possible.

All the Seminar is videotaped and will be kept in the arkives of the Departments of Physics of the University of Pavia. This will make available to those interested, also the valuable photografic material which was not provided with the printed version of the talks. This allowed dr. Silvia Cerlesi to reconstruct a summary of dr. Fischmann's talk.

Warm thanks are due to mr. Luigi Valla and Edgardo D'Uscio who take care of the videotape.

At this point, it is a pleasure to take the opportunity of having the floor, to welcome our distinguished foreign friends, whose contributions will be inequalled.

Finally, thanks are due to the Rector of the University for having made the distinguished "Aula Scarpa" available to us.

Last but not least, I personally wish to thank my closest collaborators dr. Silvia Cerlesi and ing. Giuseppe Belli for the most valuable and open collaboration given in any moment of my activity in the field of dioxin.

TABLE I: SUMMARY OF INDUSTRIAL CHEMICAL ACCIDENTS

	PERSONS		BRIEF DESCRIPTION
YEAR	EXPOSED	SITE	OF THE EFFECTS
1949	250	Monsanto plant in Nitro West Virginia	122 chloracne cases; 32 deaths, while 46.6 were expected. No excess deaths from malignant neoplasms or circulatory desease observed.
1953	75	BASF plant in Ludwigshafen (FRG)	55 chloracne cases[42 severe] 17 deaths while 11 to 25 were expected. Four gastro-inte- stinal cancers and 2 oat-cell lung cancers. Most common in- juries: impaired senses and liver damages.
1956	not given	Rhone-Poulenc plant in Grenoble	17 chloracne cases; elevated lipid and cholesterol level in blood.
1966	not given	"same"	21 chloracne cases.
1963	106	N.V. Philips plant in Amsterdam	44 chloracne cases[42 severe]; 21 had internal damage or central-nervous-system disturbances; 8 deaths, 6 possible myocardic infartion. Symptoms of fatigue observed.
1964	61	Dow Chemical plant in Midland Michigan	49 chloracne cases; 4 deaths while 7.8 were expected; 3 cancer deaths, 1.5 expected; [1 of soft tissue sarcoma].
1965-6	9 78	Spolana near Prague; con- tinuous leak	78 chloracne cases; 5 deaths. Some 50 workers observed for over 10 years; hypertension, elevated lipid and cholesterol levels in blood; prediabetes; severe liver and neurological damages.
1968	90	Coalite and Chemical plant in Derbyshire	79 chloracne cases; 1 death from coronaris thrombosis
1976	156	Icmesa plant Seveso, Italy	More than 500 residents treated for possible toxic symptons. Confirmed 134 chloracne cases. Overall normal mortality observed.

Armon F. Yanders

Environmental Trace Substances Research Center University of Missouri Columbia, Missouri Mo 65203

DIOXIN IN MISSOURI

Missouri is sometimes referred to as "The Dioxin Capital of the United States." It's not that we have more dioxin than any other state, for we probably do not: estimates of the total amount produced in the state range between 50 and 150 pounds, and I suspect that several other states will be found to exceed this by a good margin. The problem in Missouri is that our dioxin, the most toxic isomer, 2,3,7,8 tetrachlorodibenzo-p-dioxin, is located in so many different sites which are inhabited. There are now more than 40 confirmed sites of dioxin contamination in Missouri, and the number may grow even larger. For the most part, the sites are located in the east central part of the state, near St. Louis, and the southwest part of the state, near Verona, where the chemical plant that produced the dioxin is located.

The dioxin was produced as an unwanted byproduct during the manufacture of hexachlorophene, an antimicrobial agent. The hexachlorophene was being manufactured in a portion of a chemical plant built by the Hoffman-Taff Company which was leased to the Northeast Pharmaceutical and Chemical Corporation, or NEPACCO. One of the final steps in the process was distillation, and the dioxin was at its greatest concentration in the residues remaining in the still. NEPACCO arranged for the disposal of these still-bottom residues with an independent contractor. Russell Bliss, a waste-oil recycler, was hired to collect the wastes, and he ultimately hauled some 18,500 gallons from the plant in Verona back to the St. Louis area. The majority of this material seems to have been mixed with waste oil in a large storage tank. During 1971 and 1972, this mixture, or in some cases possibly

the undiluted wastes themselves, were used as sprays for the control of dust on roads, parking lots, and horse arenas.

One arena which was sprayed was at the Shenandoah Stables, north of Interstate 70 in east central Missouri. On May 25, 1971, the dirt floor inside the arena was saturated with what may have been undiluted still-bottom wastes. The next day a horse became ill, and within a week, five more. In the next few weeks, horses died, cats and dogs died, and hundreds of birds were found dead. The horses that were affected lost hair and became exceedingly emaciated. An autopsy of one showed "emaciation, dermatitis on both hind fetlocks, diffuse supporative pleuritis, and ulcerative gastritis." Various veterinarians, as well as toxicologists from the Centers for Disease Control (CDC), were unable to identify the toxic agent.

At this point, only a few people in Missouri were aware there was a problem. The owners of Shenandoah Stables certainly were, for they lost, in final count, some 62 horses that died or had to be destroyed, and the two daughters of one of the owners, Judy Piatt, became quite ill after playing in the arena in the summer of 1971. For the next year, Judy Piatt and Frank Hamphill, the other owner, followed Russell Bliss's trucks and compiled a list of the places they sprayed, as well as a list of the companies from which Bliss received other wastes. This list was sent in late 1972 to the Environmental Protection Agency (EPA) in Washington, to the CDC in Atlanta, and to the Missouri Division of Health. Times Beach was on the list. None of the agencies responded.

In July, 1974, CDC successfully identified the toxic material in a sample of soil from Shenandoah Stables as dioxin; until then it had been a mystery. CDC informed the Missouri Division of Health of its findings, and the Division of Health called Bliss, who said he had no idea where it might have come from. CDC investigation finally traced it to NEPACCO. In 1975, some soil from other sites that CDC tested also proved to have dioxin, and they informed the newly formed (1974) Missouri Department of Natural Resources. That department took no action, relying on evidence cited by CDC that the half-life of dioxin was one year or less, and assuming that time would take care of the problem of contaminated soil, if it had not already done so.

Besides, the state's main concern at that time was a large tank of liquid waste heavily contaminated with dioxin that had been found at the chemical plant near Verona, now owned by the Syntex Company. It contained 4,300 gallons of still bottoms and an estimated 13 pounds of dioxin. Finding a way to dispose of this was to preoccupy the state for several years. The Syntex Company did successfully treat the liquid, removing more than 99 percent of the dioxin by a photolytic process, but the contamination in the rest of the

state did not abate.

During the early 1980's, EPA had been quietly sampling some Missouri sites, and was coming to the conclusion that the original estimate of dioxin's half-life of one year was grossly in error. The agency asked the owners of some of the more highly contaminated sites to avoid exposure and to close their horse arenas voluntarily. Only a few people had been warned of the problems when an environmental group based in Washington released a list leaked from government agencies of over 50 potentially contaminated sites in Missouri, 14 of them confirmed. One of the potential sites was Times Beach. The publicity resulting from this news was intense.

Sampling of the potential sites began on November 30, 1982, at the largest one, Times Beach. Wearing their protective "moon suit" gear, the EPA completed sampling on December 3rd, when the sampling team was told it had to leave because of an impending flood. One said, "Migod, this town can't flood!" But the next day began the largest flood in Times Beach history. The Meramec River crested at 22 feet over flood stage, inundating the town.

Before the flood, Times Beach was a pleasant, lower-middle class community with over two thousand inhabitants. It had suffered from floods before, but as the people began to move back to their homes and businesses in late December, they found that many homes and businesses were not just damaged, they were ruined. Furthermore, they learned that an analysis of the soil beneath some streets showed traces of dioxin. People in Times Beach had arranged for this analysis with funds they had raised themselves because they felt they weren't getting answers from EPA or CDC. Nevertheless, they began to clean up their town with the full expectation of resuming normal living again. They were wrong, and for many of them began a nightmare which still continues.

At this point, just before Christmas, 1982, things began to move much more rapidly. Rita Lavelle, assistant administrator of EPA, finally released the laboratory reports that showed high levels of dioxin in Times Beach. On December 23rd, CDC relayed an advisory to the Missouri Division of Health recommending that people stay out of Times Beach. Residents who were temporarily relocated because of the flood were discouraged from moving back. Residents who had already begun to move back were encouraged to leave. This news, which was released by the Division of Health, reached many of the residents at the town's annual Christmas party in City Hall. It was crushing news, perhaps even more so because of the timing.

Times Beach immediately became notorious. For a month or two, anyone in the nation who read newspapers or watched television received regular doses of news about Times Beach. Pressures for EPA to do something mounted in Washington. In response to this pressure, on February 22, 1983, the EPA administrator came to St. Louis to announce that the government would pay 90% of the \$36.7 million necessary to buy out Times Beach. The state of Missouri was to provide the remaining 10%. This action probably would not have been taken if Times Beach had not attracted the attention of President Reagan. It was the only dioxin site in Missouri which did.

Pressures in the state of Missouri were also mounting, and the Governor, who had been relying on dioxin advice from key state government officials, appointed a Task Force on Dioxin with the charge to "recommend a practical and effective plan of action for implementing comprehensive and permanent solutions to the public health and environmental problems caused by dioxin in Missouri." The Task Force was composed of prominent citizens, and included physicians, scientists, lawyers, industry executives, and concerned citizens. The Task Force heard evidence from many sources, including EPA,

CDC, the Veterans Administration, and representatives of the Special Office in Italy that directed the cleanup program after the Seveso incident. The Task Force worked rapidly, and its Final Report was released in October, 1983.

The Final Report included three major recommendations, as follows:

- "I. The Task Force recommends that secure central storage of Missouri's soil contaminated with dioxin exceeding acceptable limits should be provided until proven technology is available to assure a comprehensive and permanent solution to dioxin contamination with minimum risk to public health and the environment.
- "II. The Task Force recommends that health studies on Missouri citizens potentially exposed to dioxin in residential, manufacturing or other occupational settings should be continued and expanded to assess the long-term public health effects due to dioxin.
- "III. The Task Force recommends that the Missouri Dioxin Strategy for secure storage of dioxin contaminated soils and for assessment of health effects, as stated in this report, be adopted and thereafter periodically updated."

In making recommendation I, the Task Force recognized that there was no proven technology for destroying dioxin in soil economically, and it will probably be many years before one is developed. At the same time, it felt that the impact on Missouri and its citizens was so great that even a temporary measure which would safely sequester the contaminated soil was better than the current situation, in which the large number of contaminated sites poses a potential threat to a large number of citizens.

Recommendation II not only suggested that health studies be expanded to include more persons, but that Missouri should participate in research on such topics as the dioxin content of human adipose tissue and its use to determine background levels due to other exposures.

The Missouri Dioxin Strategy set forth in recommendation III consists of a set of eleven specific components and provisions. Those of greatest interest to this symposium include the following four, none of which has yet

been implemented:

(1) "High priority should be given to the siting for and construction of a central storage facility and interim storage as required."

In addition to geological factors, criteria for the site selection included State ownership, exclusion of parks and wilderness areas from consideration, and utility of the site following closure of the facility. Preliminary sketches of the kind of storage bunker that would be required incorporated some of the design features of the Seveso structures. This recommendation has met with a great deal of opposition in the Missouri legislature, and there is some doubt now as to whether a central storage facility ever will be politically acceptable.

(2) "A primary aim should be the reconstruction and reinhabitation of all sites."

The Task Force felt that it was not enough that the sites simply be cleaned up, but that the integrity of the affected neighborhoods and communities be maintained, and the financial burden to the people minimized. It was recognized that the site residents have already had their lives disrupted and have been subjected to severe emotional stress, problems which are not solved by property purchases.

(3) "The experience gained at Seveso, Italy, should be utilized to the extent possible."

The Task Force was impressed by the way the Lombardi Government and the Seveso authority had addressed the problem, and recognized that Italy has developed much information on worker protection, sampling techniques and construction engineering which is directly

applicable to the Missouri situation. It pointed out that one of the problems encountered in Italy was the delay in obtaining analyses during excavation, and recommended that the state address this before any excavation begins.

(4) "The residual level of dioxin allowed to remain after excavation and decontamination must be specified."

The Task Force suggested that the Centers for Disease Control establish permissible levels of cleanup which would permit unrestricted use of residential and agricultural properties, and further suggested that other, presumably higher, residual levels might be permissible for restricted use in commercial and industrial settings.

What is happening now to Times Beach? The Corps of Engineers is working on a levee to protect the area from the strongest river currents in case another flood occurs. The City Hall was destroyed by a fire, probably started by vandals, and the city government has set up shop in a trailer just outside the entrance to Times Beach. Homes, businesses, and churches are abandoned, and tall weeds are replacing the grass and flowers that used to be there. It is not uncommon to see wild deer in the streets: they seem to have discovered that there are few intruders in the town, because only one house is still occupied and the only access road is controlled by 24-hour security guards. But one still can find painted signs on buildings such as one over a garage door showing the high water mark of the flood ("The Big One-'82"), or one on a house which, misspellings and all, conveys the despair of the homeowner ("For Sale to U.S. Goverment - I losted my family because of DIXION - There's no one to take care of me now".)

For the time being, Times beach and most of the contaminated sites in Missouri remain on "hold". The buyout of Times Beach is not yet complete, and there is no consensus as to what will be done with the town when it finally belongs to the State. In Southwest Missouri, the EPA mobile incinerator has had a successful burn, and the liquid wastes remaining after the cleanup by Syntex have been destroyed. A few cubic yards of contaminated soil have also been successfully incinerated. At a few sites near St. Louis, the contaminated soil is being excavated and replaced with clean soil, with the contaminated material to be stored indefinitely.

Times Beach has also become the center of a new activity. Following the recommendation of a Research Advisory Committee, which was formed with the cooperation of the Missouri Department of Natural Resources and the University of Missouri, the State of Missouri has established a Dioxin Research area at Times Beach. A major objective of this project is to identify methods which have the greatest potential to detoxify dioxin-contaminated material, and to evaluate those methods which appear to be successful. Perhaps the research done at this site will make Missouri "The Dioxin Capital of the United States" for its contributions to solving a problem that impacts on us all.

Terry L. Stoddart

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DEMONSTRATION OF INNOVATIVE REMEDIAL ACTION TECHNOLOGIES AT UNITED STATES MILITARY DIOXIN CONTAMINATED SITES

ABSTRACT

The United States Air Force is currently seeking to resolve problems associated with soils contaminated with 2,3,7,8-tetrachlordibenzo-p-dioxin (dioxin). Air Force use of the phenoxy herbicide formulation known as Herbicide Orange has resulted in soil contamination of three military sites in the Continental United States. To resolve these problems, the U.S. Air Force Engineering and Services Laboratory and its prime contractor, EG&G Idaho, have initiated a research program to evaluate, under field conditions, technologies that may reduce the level of dioxins in contaminated soils. Two pilot-scale technologies: (1) advanced electric reactor, developed by the J.M. Huber Corp., Borger, Texas, and (2) thermal desorption/U.V. destruction, developed by the I.T. Corp., Knoxville, Tennessee, have been tested at a military installation in the Southeastern United States. Although independent confirmation of technology success is pending, preliminary test results indicate that both technologies are capable of reducing the levels of dioxin in contaminated soils from 240 parts per billion to less than 1 part per billion. These data suggest that either of the technologies could be employed for full-scale site restoration. Field trials of two additional technologies are scheduled for late 1985.

1. INTRODUCTION

BACKGROUND

In April 1970, the Secretaries of Agricolture; Health, Education, and Welfare; and the Interior jointly announced the suspension of certain uses of 2,4,5-trichlorophenoxyacetic (2,4,5-T). This suspension resulted from published studies indicating that 2,4,5-T was a teratogen. Subsequent studies revealed that the teratogenic effects resulted from a toxic contaminant in the 2,4,5-T, identified as 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)*.

Subsequently, the Department of Defense suspended the use of Herbicide Orange (HO), which contained 2,4,5-T. At the time of the suspension the Air Force had an inventory of 1.37 million gallons of Herbicide Orange in South Vietnam and 0.85 million gallons at the Naval Construction Battalion Center (NCBC), Gulfort MS. In September 1971, the Department of Defense directed that the HO in South Vietnam be returned to the United States and that the entire 2.22 million gallons be disposed in an environmentally safe and efficient manner. The 1.37 million gallons of HO in South Vietnam were moved to Johnston Island (JI), Pacific Ocean in April 1972. The average concentration of dioxin in the HO was about 2 parts per million with the total amount of TCDD in the entire HO stock estimated at 44.1 pounds.

⁻ The word "dioxin" in this report refers to 2,3,7,8 - TCDD.

Herbicide Orange is a reddish-brown to tan liquid, soluble in diesel fuel and organic solvents, but insoluble in water. One gallon of HO theoretically contained 4.21 pounds of the active ingredient 2,4-D and 4.41 pounds of the active ingredient 2,4,5-T. Herbicide Orange was formulated to contain a 50:50 mixture (by weight) of the n-butyl esters of 2,4-D and 2,4,5-T. The percentages of the formulation typically were:

n-butyl ester of 2,4-D	49.49
free acid of 2,4-D	0.13
n-butyl ester of 2,4,5-T	48.75
free acid of 2,4,5-T	1.00
inert ingredients (e.g., butyl alcohol and ester moieties)	0.63

Various disposal techniques for Herbicide Orange were investigated from 1971 to 1974. Destructive techniques included soil biodegradation, high-temperature incineration, deep-well injection, burial in underground nuclear test cavities, sludge burial, and microbial reduction. Techniques used to recover a useful product included activated charcoal filtration, return to manufacturers, fractionation, and chlorinolysis.

Of these techniques, only high-temperature incineration was sufficiently developed to warrant further investigation. The other methods were rejected because of several considerations, including long lead times for development, inadequate assurance of success, and the lack of industrial interest.

During the summer of 1977 the United States Air Force (USAF) disposed of 2.22 million gallons of HO by high-temperature incineration at sea. This operation, Project PACER HO, was accomplished under very stringent regulation by the U.S. Environmental Protection Agency (EPA) ocean-dumping permits.

Following the at-sea incineration the Air Force Engineering and Services Center established a research and monitoring program to:

- (1) Define (Map) levels of dioxin contamination at Air Force Sites.
- (2) Develop or identify innovative treatment technologies for removing dioxin from contaminated soils.
- (3) Conduct pilot-scale demonstrations (field evaluations) of developed or identified remedial action technologies.

2. DESCRIPTION OF AIR FORCE DIOXIN-CONTAMINATED SITES

2.1 JOHNSTON ISLAND, PACIFIC OCEAN (JI)

Johnston Island, a coral atoll, controlled by the Department of Defense (DoD), is located 750 nautical miles southwest of Honolulu in the central Pacific Ocean. The island is 1/2 mile wide and 2 miles long, with a mean elevation of 7 feet above sea level. The majority of the island was constructed from coral dredged from the atoll lagoon. The island has no freshwater supply and receives approximately 15 inches of rain per year. The island lies in the tradewind zone and the average wind speed is

20 miles per hour. The total island population is approximately 500 personnel.

Ten acres of Johnston Island served for storage and support operations for 1.27 million gallons of Herbicide Orange returned from South Vietnam. The operational areas included de-drumming, drum crusher and decontamination facilities. Historical data indicate that surface soils at the former storage site are contaminated with Herbicide Orange and the associated dioxin contaminant. The levels of 2,3,7,8 TCDD contamination ranged from less than 0.01 parts per billion (ppb) to 250 ppb. Although the bulk of TCDD contamination can be found in the first 40 cm trace levels have been detected to 144 cm.

2.2 NAVAL CONSTRUCTION BATTALION CENTER, GULFPORT, MS (NCBC)

The NCBC is located in Gulfport, MS. The NCBC is located approximately 2 miles from the Gulf of Mexico and occupies a land area of several square miles. The NCBC is approximately 20 feet above sea level. The soil is sand to sandy loam, intermixed with some clay.

Approximately 18 acres at the NCBC served as a storage site for 0.85 million gallons of Herbicide Orange. The "old" storage site was stabilized with Portland cement approximately 30 years ago. The stabilized soil provided a hardened storage area for

[&]quot; Parts per billion (ppb) = ug/kg

heavy supplies and equipment. Over the years, additional fill material (shell, rock, soil, asphalt, and road oil) was added to the storage area, providing a cover of several inches over the cement-stabilized soil.

Approximately 12 acres of the 18 acre site are considered contaminated with herbicide orange and its associated dioxin. During 1980, sediment retention basins were constructed on the storage site to prevent the migration of dioxin-contaminated soils off-site. Currently, the "old" Herbicide Orange storage site is a restricted area and is not used. Historical data indicate that surface soils at the former storage site are contaminated with Herbicide Orange and its associated dioxin. The levels of 2,3,7,8 TCDD contamination range from less than 0.01 ppb to 350 ppb. A single depth profile collected from an area of known contamination indicated that the majority of 2,3,7,8 TCDD is located within the first 24 cm. However, trace levels of dioxin were detectable to a depth of 70 cm.

2.3 EGLIN AFB, FL

The Eglin AFB Reservation is located in Northwest Florida and covers approximately 750 square miles. To the South, the Reservation is adjacent to Choctawhatchee Bay and the Gulf of Mexico, while the North and East are bordered roughly by the Yellow River and Alaqua Creek.

The Reservation lies on generally level or gently rolling terrain, all under 300 feet elevation and sloping to sea level on the West and South. It is drained by small tributaries of the Yellow River and Alaqua Creek and by smaller streams that flow directly into Pensacola and Choctawhatchee Bays. The valleys of these streams are steep-sided and end abruptly. The soil on most of the Reservation consists of excessively drained, deep, acid sands of the Lakeland series.

Hardstand 7 is an asphalt and contret aircraft parking area located west of the north-south runway on the main Eglin airdrome, approximately 65 feet above sea level. Hardstand 7 was of the three areas on Eglin that had been previously used for storing and loading military herbicides. Hardstand 8 and the East end of Tailway 9 were relatively free of dioxin residues in the soil. Hardstand 7 was the most extensively used site for herbicide storage and loading during the 1962-1970 spray test program. The soil of this area is sandy, with good drainage properties. Directly behind the hardstand is a ravine that drops off approximately 50 feet to a small pond, called Hardstand Pond. Because of the packing caused by vehicular traffic and the water-repellent nature of the oil-based herbicude contamination, runoff of excess water caused erosion in some spots, leading to the frequent use of fill dirt. Eventually, an asphalt-covered dike was constructed on the rim of the ravine for soil stabilization and a storm drain was installed for erosion control.

The levels of 2,3,7,8-TCDD contamination ranged from 0.01 ppb to 350 ppb. Depth of penetration studies collected from an area of known contamination indicated that the majority of 2,3,7,8-TCDD contamination is located in the first 161 CM. However, trace level of dioxin were detectable to a depth of 430 CM.

3. OVERVIEW OF THE CURRENT RESEARCH PROGRAM

3.1 INTRODUCTION

The Air Force dioxin research program can be divided into three categories:

- a. Basic Research; phenomena investigation
 - (1) High Risk
 - (2) Long-Term pay-off
- b. Pilot testing and prototype development
 - (1) Moderate risk
 - (2) Short-term pay-off
 - (3) Develop cost and scale-up factors
- c. Environmental Monitoring
 - (1) No risk
- (2) Required to define levels of contamination in various environmental media, to support basic research and pilot testing.

3.2 BASIC RESEARCH PROGRAM

Project: In-Situ Biodegradation (Genetic Engineering)

Principal Investigator: Dr. Jack Loper Institution:

University of Cincinnati Medical School

Sponsor: U.S. Environmental Protection Agency and the Air

Force Engineering and Services Center.

Objective: Employ recombinant DNA technology to develop a microorganism (yeast) capable of degrading polychlorinated organic compounds including 2,3,7,8 TCDD. Research based on the cytochrome p-540 monooxygenase enzyme system found in eucaryotic organisms.

Project: Dechlorination of Aromatic Compounds by Anaerobes

Principal Investigator: Dr. Jim Tiedje

Institution: Michigan State University

Sponsor: Air Force Engineering and Services Center

Objective: Isolate, identify and characterize anaerobic microbial populations that metabolize chlorinated aromatic compounds including 2,3,7,8-TCDD. Research is based on the screening of environmental samples to detect anaerobic metabolic activity with subsequent elucidation of biochemical mechanisms and controlling environmental factors.

3.3 PILOT TESTING AND PROTOTYPE DEVELOPMENT

Project: In-Place Chemical Decontamination of Soil

Principal Investigators: Mr. Robert Peterson

Contractor: Galson Research Corporation

Sponsors: U.S. Environmental Protection Agency and the Air Force Engineering and Services Center.

Objective: Develop techniques to effectively apply the chemical reagent Potassium hydroxide and polyethylene glycol (KOH/PEG) to dioxin contaminated soil in order to achieve decontamination. Secondly, conduct field demonstration of the best application technology.

Project: Herbicide Orange Incinerator Studies

Principal Investigator: To be determined

Prime Contractor: EG/G Idaho

Sub Contractor: To be determined

Sponsor: Air Force Engineering and Services Center

Objective: Determine the feasibility of employing a full-scale rotary-kiln incinerator to decontaminate large quatities of soil contaminated with 2,3,7,8 TCDD. Secondly, develop cost and reliability factors based on field demonstration.

Project: <u>Site Demonstration: Environmental Restoration</u>
Technologies

Principal Investigators: Mr. Harry Williams, EG&G Idaho; Mr. Darrell Derrington, J.M. Huber Inc., Dr. Bob Fox, IT Corp.

Prime Contractor: EG and G Idaho

Sub Contractors: J.M. Huber Corp and IT Corp

Sponsor: Air Force Engineering and Services Center

Objective: Demonstrate (field test) unique, cost-effective, restoration technologies at 2,3,7,8 TCDD contaminated sites. Secondly, develop cost and scale-up factors for full-scale equipment. Technologies selected for demonstration are (1). Advanced Electric Reactor, J.M. Huber Corp and (2) Therm Thermal Desorption/U.V. Destruction, IT Corp.

3.4 ENVIRONMENTAL MONITORING

Project: Herbicide Orange (dioxin): Soil Mapping and Ground
water Survey

Principal Investigators: Mr. Harry Williams, EG&G Idaho; Mr. Al Tordini, U.S. Testing; and Mr. Lou Adams, Ecology and Environment.

Prime Contractor: EG&G Idaho

Sub Contractors: U.S. Testing, Ecology and Environment

Sponsor: Air Force Engineering and Services Center

Objective: Map the location and extent of 2,3,7,8 TCDD contamination at three Air Force contaminated sites. Also to determine the depth penetration of TCDD and define the best location for placement of groundwater monitoring wells.

4. PILOT SCALE TECHNOLOGY DEMONSTRATION

4.1 BACKGROUND

The Air Force Engineering and Services Center established a research program to evaluate the most promosing, unique and currently available environmental restoration technologies via

field test at military dioxin contaminated sites. To accomplish this task the Air Force Engineering and Services Center established a prime contractor relationship with EG&G Idaho (Idaho National Engineering Laboratory). EG&G selected two technologies for demonstration at military sites. These technologies are: (1) Advanced Electric Reactor, developed by the J.M. Huber Corp, Borger, TX, USA, (2) Thermal Desorption/U.V. Destruction, developed by IT Corp, Knoxville, TN, USA. Both technologies have been evaluated by field test at a U.S. Navy facility in Gulfport, Mississippi. Preliminary results of these tests will be described later.

4.2 TECHNOLOGY SUMMARY AND PROCESS DESCRIPTION

(1) Advanced Electric Reactor

The Advanced Electric Reactor uses a technology which rapidly heats feed materials to temperatures in the range of 4000° to 4500°F, with surface heating rises up to 10⁷⁰F per second using intense thermal radiation in the near infrared region. Feed stock is isolated from the reactor core by means of a nitrogen blanket. Pyrolysis occurs since no oxygen is present.

The solid feed is gravity-fed through the reactor where pyrolysis occurs. After leaving the reactor, the product gas and waste solids pass through a postreactor treatment zone (PRTZ). Solid-and gas-phase residence times for both the reactor and the PRTZ can be independently varied to achieve essentially any

desired destruction efficiency. The PRTZ is water cooled and provides additional residence time; however, its primary function is to cool the molten soil particles below their fusion temperature to avoid coagulation in the treated solid waste bin and to cool the gas prior to downstream particle cleanup.

The detoxified solid material exiting the PRTZ is, for the most part, collected in a solids bin which is sealed so the atmosphere. The off-gas is then conveyed to a bag filter for removal of any remaining fine soil residuals.

The process gas cleaning train consists of activated carbon beds for the removal of any trace level residual chlorine or organics. The cleaned gas (composed almost entirely of nitrogen and water vapor) is then emitted to the atmosphere. The low process gas flow rate (about 5 scfm) economically allows a high degree of cleanup.

(2) Thermal Desorption/U.V. Destruction

The thermal desorption process involves passing the contaminated soil through a thermal treatment unit operating at temperatures around 500°C. By the process of evaporation, dioxin and other organics are volatilized, collected in an organic solvent, and destroyed by U.V. photolysis.

Contaminated soil will be collected, crushed to proper size if necessary, and placed in storage drums. This material will be fed at a controlled rate by a screw feeder into a rotary drum

unit that is heated on the shell of an external gas fired furnace. The drum rotation speed and slope are controlled to provide the required soil residence time. The treated soil discharged from the drum is collected in a closed drum. The soil test feed rates will be in the range of 20 to 100 pounds per hour.

The rotary drum is kept under slight negative pressure and is swept continuously with a nitrogen gas stream to carry off the desorbed materials. The carrier gas is quenched and scrubbed by a cooled, recirculated stream of a high boiling hydrocarbon solvent to remove the desorbed materials. Any build-up of the carrier gas due to inleakage or soil material decomposition will be vented through an activated carbon bed. The carrier gas will also be monitored for oxygen content. Solid fines that collect in the quench solvent will be filtered for separation and analysis.

The hydrocarbon solvent will accumulated desorbed material from several desorption tests before being processed for organic destruction. When the hydrocarbon solvent is adequately loaded, it will be batch processed in the UV photolysis reaction by recirculation. Treatment time is expected to be about 24 hours.

After each desorption test, any accumulated water in the quench solvent will be separated and treated with activated carbon.

4.3 FIELD TEST PROTOCOL

A suitable feedstock matrix was collected from the contami-

nated site at NCBC.. The feedstock consisted of approximately the following:

80 percent cement-stabilized soil

10 percent oyster shell

5 percent pea gravel

5 percent asphalt and road oil

The materials were reduced in size to accomodate the requirements of the two technologies. The total volume of feedstock was combined by ring and cone mixing and homogenized with a portable cement mixer. Replicate analysis of the feedstock indicated an average 2,3,7,8, TCDD concentration of 240 ppb. The Advanced Electric Reactor and the Thermal Desorption/U.V. Destruction devices treated approximately 1000 pounds and 2500 pounds respectively. The field tests were accomplished incrementally according to different treatment conditions. The test program was initiated at the NCBC on 20 May 1985 and was concluded on 30 June 85. Results of comprehensive laboratory analysis on the treated materials are pending. Preliminary test results follow.

5. FIELD TEST PRELIMINARY ANALYTICAL RESULTS

- 5.1 Advanced Electric Reactor 3700⁰ at 37 pounds/hr feed rate
 2,3,7,8 TCDD (Feedstock) 240 ppb (EPA/CLP procedure)
 2,3,7,8 TCDD (treated soil) 0.04
- 5.2 Thermal Desorption/UV Destruction

Five desorption tests were performed at different conditions

of operating temperature and feed rate (and associated soil residence time). Operating (soil) temperatures ranged from 560^{0} C to 460^{0} C (Run 5). Soil feed rates ranged from about 30 lb/hr to about 100 lb/hr.

The analytical results for 2,3,7,8-TCDD area as follows:

2,3,7,8-TCDD Concentration (ppb)

Run No.	Feed Soil Method 1	Treated Soil Method 1 Method 2
1	232	ND(1.3)
2	249	ND(0.84) ND(0.85)
3	242	ND(1.9) ND(0.53)
4	272	ND(0.49)
5	256	0.91

Analytical detection limits are given in parenthesis for nondetected (ND) results: Method 1 refers to the standard EPA-CLP extraction procedure (jar using methanol/hexane). Methods refers to an alternative extraction procedure (acid treatment followed by Soxhlet extraction with benzene).

6. SUMMARY

The Air Force Engineering and Services Center has established a comprehensive research program to identify or develop techniques that can be employed to reclaim sites contaminated with 2,3,7,8 TCDD. Preliminary results from two field trails indicate that the Advanced Electric Reactor and the Thermal

Description/U.V. Destruction technologies may be useful for dioxin site restorations. Comprehensive chemical analyses of feedstock and treated soils are pending. A final evaluation of the two technologies will include cost per unit of soil treated as well as engineering scale-up factors.

7. FUTURE ACTIVITIES

A second field trail of the Thermal Desorption/U.V. Destruction technology (IT Corp) is scheduled for Johnston Island during October and November, 1985. A demonstration of a full-scale rotary kiln incinerator is scheduled for Johnston Island March-July 1986. The full-scale trial will involve treatment of up to 7000 cubic yards of dioxin-contaminated soil.

Field trial of the potassium hydroxide/polethylene glycol reagent is planned for early 1986.

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TIMES BEACH DIOXIN RESEARCH FACILITY

ABSTRACT: This paper describes two successful experiments for destroying dioxin at the Times Beach Dioxin Research Facility in Missouri and explains the analytical results obtained as of October 1985.

Missouri's experience with dioxin has been characterized by a unique set of circumstances and events that affected a large number of our citizens. This environmental dilemma posed a technical and waste management challenge of unprecedented magnitude. The Missouri Department of Natural Resources faced this challenge at a time when there were few answers. Questions concerning possible health effects from exposure to various levels of dioxin; questions about removing the contaminant from soils, rocks, and brush; questions concerning the destruction of dioxin - all remained unanswered. In many cases we were faced with theories, assumptions, and inconclusive data.

A unique opportunity to fill the knowledge gap was created when our department established the Times Beach Dioxin Research Facility. This facility offers scientists and engineers a chance to stand on the frontier of science by filling in this gap.

Historically, the contamination of Missouri's 44 confirmed sites has been traced to improper disposal of chemical waste from a now-defunct firm, the Northeastern Pharmaceutical and Chemical Co. This company manufactured hexachlorophene and created dioxin as a waste byproduct. The dioxin contaminated the company's thousands of gallons of waste still bottoms, industrial sewage, and sludge.

A used-oil transportation firm, the Bliss Waste Oil Co., contracted to remove much of the still bottoms. After mixing the chemical waste with other salvaged oil, this transportation firm sold the waste as fuel oil or sprayed it to control dust on dirt roads, parking lots, and horse arenas.

Other dioxin-contaminated waste from Northeastern Pharmaceutical was buried on farms or sent to a wastewater treatment school - sites where they remained untreated. These disposal sites, plus the sprayed oil

sites, make up the 44 dioxin-contaminated sites in Missouri identified as of October 1, 1985. The greatest health hazard occurred at the sites where the dioxin-tainted oil was sprayed for dust control. This practice escalated the dioxin problem by introducing the chemical to areas where thousands of citizens resided. In these areas, dioxin levels ranged from less than one part per billion to as high as 1,800 parts per billion.

In December 1982, Missouri's dioxin problem gained world attention when more than 800 families were warned to stay out of their homes in the eastern Missouri town of Times Beach.

The dioxin problem prompted Missouri's Governor to create a Dioxin Task Force that was charged with finding technologies for destroying dioxin. In October 1983 the task force concluded that no technologies were available and that it would be several years before suitable technologies were developed.

So the major goal of the task force and the department became, and still is, to find ways to destroy the dioxin contamination.

The company that inherited the problem from Northeastern Pharmaceutical, Syntex Agribusiness, also worked to achieve this goal. Syntex developed a photolysis process that destroyed much of the dioxin in the contaminated waste. In this process, hexane was used as a solvent to absorb the dioxin from the waste oil. The hexane solution was then exposed to high-intensity ultraviolet light to destroy the dioxin molecule. Although this photolysis process worked well on the waste oil. it was not considered an appropriate technology for contaminated soil.

In an attempt to find a temporary solution to the problem of contaminated soil at Times Beach, the United States Environmental Protection Agency and the state of Missouri proposed a plan to contain and secure the contaminated soil until a method of destruction could be found. But, during the public-hearing process, many concerned citizens urged us to find a technology for dioxin decontamination other than containment and urged us to explore in-situ treatment. The extreme variability of soil contamination at the various sites, the types of soil,

and many other factors made this task a difficult one.

To address this challenge of finding a suitable dioxin-destroying technology, the Missouri Department of Natural Resources created the Times Beach Dioxin Research Facility to provide a set of controlled conditions. This facility serves as an available site for researchers to test and compare their technologies.

A committee formulated a plan and established guidelines for the use of the research facility, which is located in the portion of Times Beach that had the highest level of contamination. The asphalt cover was removed from the roadway, and the contaminated soil was excavated and then processed to assure a uniform sample. The processing consisted of screening the material to one-half inch; transferring it to a 10-cubic-yard cement truck; operating the cement mixer for six to eight hours during the filling process; recompacting the 10 cubic yards into three identical stainless-steel bins, six by eight by two feet; and then compacting to 80 percent of the nominal density.

The resulting construction project yielded 61 research units that consisted of 20 sets of three identical units and one control unit.

The research facility is supported by the addition of water and electricity at each of the soil bins. An observation trailer, from which the state can observe all research activities, and a decontamination trailer, from which researchers can change from their street clothes into protective clothing and equipment, are part of the facility along with on-site storage and showers. There also is a soils laboratory for the preparation of samples. An off-road vehicle and trailer are available for transportation of equipment, and a high-pressure steam cleaner is available for the decontamination of equipment.

This unique research facility was opened July 30, 1984, and has been used by a number of scientific companies in the quest for a dioxin-destroying technology.

Two technologies already have proven successful on a small scale. They are the J. M. Huber and Shirco processes.

In November 1984, J. M. Huber brought in an advanced electric reactor for testing. And on November 13, Huber demonstrated that its high-temperature thermal treatment device was capable of destroying dioxin in contaminated soil.

The Huber process utilizes a theory of raising the temperature of the finely ground contaminated soil to approximately 4,500 degrees Fahrenheit in a non-oxidizing environment. The advanced electric reactor consisted of a three-inch graphite tube that was heated externally by electrodes radiating at temperatures of 5,000 degrees Fahrenheit; the graphite tube subsequently reached temperatures of approximately 4,800 degrees Fahrenheit. A nitrogen blanket kept the falling soil from impacting the side of the graphite tube and the organic material in that soil broke down into its molecular constituents in the process of heating up. The soil formed into a liquid and then reconverted to a solid as it went through a cooling chamber. The solid material was tested after it was thermally treated. There was no detectable dioxin in the treated soil. The unit that was tested at the Times Beach facility treated approximately 100 pounds of soil in one day.

The exhaust gases from the Huber reactor went to a bag-type dust collector and also to a carbon absorption unit where any material that theoretically could escape was finally collected before gases went into the atmosphere.

The second process to prove successful was conducted on July 10, 1985, by Shirco, Inc. The company brought in a portable infrared heating system that demonstrated the capability of reducing the dioxin levels in the soil below one part per billion.

This particular system consisted of a moving metal belt where the soil, approximately two inches deep and three feet wide, was placed. The soil passed underneath electric infrared heating electrodes that raised the temperature of the soil to approximately 1,600 degrees Fahrenheit. The dioxin and organic molecules were driven off the soil in a vapor phase, and the exhaust gases were then collected and sent to an

afterburner where the temperature was raised to greater than 2,200 degrees Fahrenheit for longer than a two-second residence time. The gases then went to a high-efficiency Venturi scrubber where any particulate and chlorine gases were absorbed into the water before being exhausted to the atmosphere.

On the same day as the test, the Shirco unit demonstrated its capability of reducing dioxin to below one part per billion. In addition, no contamination was detected in the exhaust gases or in the dust from the air pollution control device.

Other technologies also are being tested at the Times Beach Dioxin Research Facility. One is a vaporization process by Monsanto Chemical Co. that involves the natural transfer of dioxin from the soil. Monsanto has demonstrated, by computer modeling and laboratory testing, that the dioxin molecule exhibits a low-vapor pressure. The company believes that vaporization may be the primary mode of environmental movement. Monsanto further believes that natural evaporation will cause the dioxin concentrations in the upper two-and-one-half inches of soil to decrease over a period of time. Once the dioxin molecule is in the atmosphere, ultraviolet light then will destroy it.

A hydrazine process is being tested by the RMC Corp. in cooperation with Agro-K Co. This test will determine whether the treatment of contaminated soil with hydrazine will destroy the dioxin molecule. Initial results have indicated no decontamination.

Another test activity currently going on is an enzyme degradation process that is being tried by Agro-K Co. This process provides an enzyme media to the research plots so natural bacteria can break down dioxin molecules. By enhancing the process with a growth media, the natural biological process may cause degradation of the dioxin molecule over time.

After four months, samples from these early experiments by Monsanto and Agro-K were analyzed without significant results.

Another company is trying two dioxin-destroying technologies. One of the technologies being tried by the Parts Per Million Co. is similar to Agro-K's enzyme degradation process. In addition, the Parts Per Million Co. is trying a process that treats contaminated soil with organic solvents. The company wants to determine if the dioxin molecule will be transported to the solvent, where it can more easily be destroyed.

All these experiments are unique in the world. They have been developed under a concept of providing a controlled site, the Times Beach Dioxin Research Facility, at which researchers can develop methods for successfully destroying dioxin.

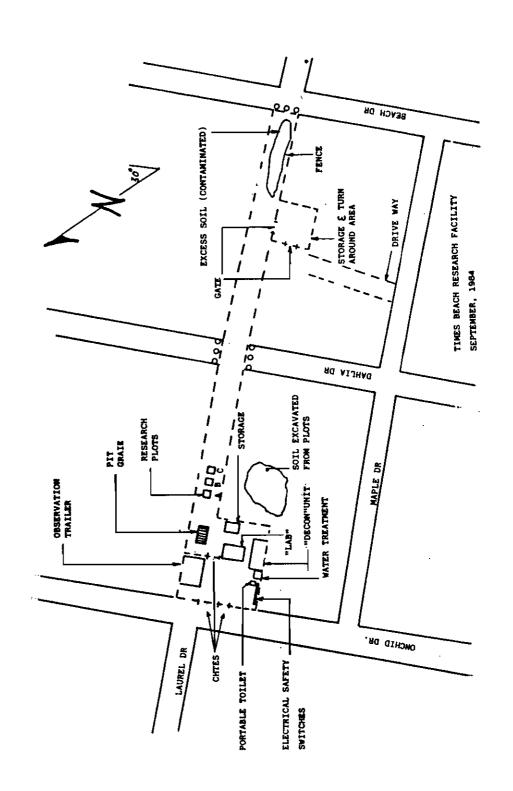
We sincerely hope that a suitable dioxin-destroying technology will result from Missouri's dioxin experience...a technology that will help all of us who must deal with dioxin contamination and its effects.

I invite all of you to come to Missouri to see our Times Beach Dioxin Research Facility and, perhaps, to use the facility to conduct research that might solve the dioxin problem.

Thank you.

SUMMARY OF TEST RESULTS

COMPANY	TECHNOLOGY	UNIT NUMBER	PRETEST CONCEN. 2,3,7,8 TCDD (PPB)	POST TEST CONCEN. 2,3,7,8 TCDD (PPB)	DATE OF POST TEST
Agro-K	Enzyme enhancement	1(a)control 1(b) 1(c)	260 220 220	217 159 314	10/31/84 10/31/84 10/31/84
		1(0)	720	314	10/31/04
PPM	Enzyme enhancement	3(a)control 3(b) 3(c)	120 120 110	NA NA NA	N A N A N A
Monsanto	Vaporization	4(a)control 4(b) 4(c) 5(a)control 5(b) 5(c)	110 110 110 180 180 170	NA NA 122 122 184 121	NA NA 10/31/84 10/31/84 10/31/84 10/31/84
JM Huber	Advanced electric reactor	Batch	120	<1	11/13/84
Shirco	Infrared incineration	Batch Batch	306 156	<1 <1	7/10/85 7/11/85
Agro-K/ RMC	Hydrazine treatment (Lab)	Betch A Batch B Betch C	52 63 48.5	42 33 61	NA NA NA



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E.P.A. RISK ASSESSMENT OF CHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS (CDDs/CDFs)

I. <u>Introduction</u>

"Environmental concern" was one of the major domestic issues in the United States during the 1960s. The nationwide observance of Earth Day in 1970, involving hundreds of thousands of people, vividly demonstrated the depth and breadth of popular feeling on the subject. In the same year, public demand for action to protect the environment and natural resources was partially answered in the formation of the United States Environmental Protection Agency (USEPA).

During the same time period, although unnoticed by most, the issue of "dioxin", specifically, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) was maturing

as well. The chemical is a contaminant in certain herbicides, including the Agent Orange that was used by US Armed Forces in Vietnam to defoliate vegetation and the 2,4,5-T that was used domestically. Just as the USEPA was being formed, the powerfully toxic properties of 2,3,7,8-TCDD were being verified in animal systems, and action was being taken to limit exposure to citizens in the United States.

However, there were environmental concerns other than 2,3,7,8-TCDD that drew most of the public attention in those early days. Specifically, among the first items of business for the new agency was a series of chlorinated insecticides; i.e.,

DDT, chlordane, heptachlor, aldrin and dieldrin. These chemicals were of concern due to their persistence in the environment and their adverse effects on human health and the environment. As the Agency developed procedures for regulating these substances, the Agency also developed methods for assessing the significance of levels of chemicals in the environment through the process known as "risk assessment".

In the late 1970s, USEPA initiated regulatory action to cancel the use of certain chemicals contaminated with 2,3,7,8-TCDD. The Agency employed its techniques of risk assessment in order to make the case that these substances presented "an unreasonable risk", meaning that the risks associated with using these chemicals outweighed the benefits of their use. Now, in the mid-1980s, the Agency continues its examination of risks posed by a panoply of CDDs/CDFs, using the methods of risk assessment in reaching regulatory decisions.

In this paper, I will discuss the basic concepts of risk assessment as practiced by USEPA, using 2,3,7,8-TCDD as a example in a hypothetical situation. The goal is to provide the reader with both an introduction to risk assessment concepts and an appreciation of USEPA's rationale for regulating CDDs/CDFs.

II. Dr. Malady's Risk Assessment of 2,3,7,8-TCDD

Professor Soma Malady of the Institute of Toxicology in Bovine, California entered his office one hot afternoon to find a glass of clear, cool water sitting on his desk, together with a note which read: "Enjoy this water. You deserve it!" Thinking

that the water must be a thoughtful gesture by an appreciative student or a grateful secretary, the Professor smiled and lifted the glass. Just as he was about to let the sparkling water slake his thirst and cool his soul...he noticed a message written in small letters at the bottom of the note: "This glass contains 2,3,7,8-TCDD, present at a concentration of 1 part per trillion (1 ppt)".

Suddenly stopping just short of putting the glass to his lips, the Professor's body became outwardly motionless, while inwardly his mind raced ahead full-speed, leading the good doctor through the four stepsof his own "risk assessment (RA)": Hazard Identification; Dose-Response Assessment; Exposure Assessment, and Risk Characterization. The first questions of Risk Assessment (RA) had flashed through his mind so quickly that the Professor was never even aware that he had asked them. However, within two milliseconds, he had completed the first step, Hazard Identification. In this process, he had asked --and unconsciously answered -- two qualitative questions: "What is in this glass?" and "Is there any reason that I should be concerned?"

The answer to the first of these questions was known, if the note was to believed; that is, 2,3,7,8-TCDD was in the glass. In less time than it took to put the glass down, Malady's mind had a provided him with the basic information he needed to answer the second question. "2,3,7,8-TCDD" is the shorthand chemical name for 2,3,7,8-tetrachlorodibenzo-p-dioxin, a chemical with a long history in toxicology and environmental protection that

gained notoriety in the decades of the 1960s, '70s, and '80s as "the most toxic chemical made by man". As an unwanted impurity associated with certain chemical processes, chemical accidents, and sources of combustion, 2,3,7,8-TCDD has been linked to such familiar Agent Orange, Sevso, Love Canal, and Times Beach. Even now, strenuous debate surrounds this chemical.

The reputation of this chemical has been earned by its observed effects in animals, which include induction of cancer, birth defects, immunological effects, and reproductive problems at very low doses, and reports associating exposure to 2,3,7,8-TCDD with certain types of cancer in humans. However, epidemiologic studies begun in the early 1980s and scheduled for completion between 1988 and the turn of the century have not yet demonstrated the presence of these adverse effects in humans. At same time, the singular toxic behavior of 2,3,7,8-TCDD in animal systems has attracted the attention of toxicologists and regulators alike. Indeed, the Professor's mental Hazard Assessment qualitatively elicited a high level of concern, much to the distress of his water-parched lips.

As he quickly, but carefully, lowered the indicted glass to the desktop, Professor Malady just as carefully addressed the second step in risk assessment -- Dose-Reponse Assessment; i.e., "Quantitatively, just how hazardous is this glass of contaminated water?" Addressing Dose-Response Assessment portion of the riksk assessment took more conscious thought by the Professor. However, now that the immediate danger of swallowing a potentially dangerous liquid had been avoided, he could take some

time in bringing his vast mental powers to bear on this more exacting question.

Reaching over his desk to the towering and overburdened bookshelf that strained at both his desk and the walls of his cramped office, Professor Malady pulled out a well-used volume entitled "Water Quality Criteria Document on 2,3,7,8-Tetrachlorodibenzo-p-Dioxin", published by the United States Environmental Protection Agency in February, 1984. The Professor eased himself down into his old wooden chair, slowly pushed himself back away from the desk to the familiar pleas of four oil-starved casters, and turned to the section on "Carcinogenicity: Dose-Response".

Here he quickly reviewed a few basic facts. First, a number of separate experiments have linked administration of 2,3,7,8-TCDD to laboratory animals and subsequent development of cancer in those animals. Second, the levels at which these experiments were run, while quite low relative to most cancer studies, were still considerably higher than the level of 2,3,7,8-TCDD allegedly present in his glass of water. Third, the USEPA and others have adopted a mathematical procedure for extrapolating from the "high" doses used in animal studies to the "low" doses likely to be encountered in environmental situations. The procedure, called by the forbidding title of the "linearized multistage extrapolation model", also attempts to account for the difference between a response seen in animals and what a similar response might be in humans.

Turning to a summary table near the back of the volume,

the Professor's eyes scanned the entries searching for the "q1*", the value derived by the model from the experimental evidence which is a measure of the potency of the chemical to cause cancer. Three quarters of the way down the page, his eyes rivetted on their target; and, unbiddened, a low whistle escaped his still parched lips as he read: "q1* = 1.57 x 10+5 (mg/kg-d)-1". He knew immediately that this arcane expression shrouded a simple message: Using this method of analysis, 2,3,7,8-TCDD is more than 100 times more potent in causing cancer in laboratory animals than any other chemical ever assessed by the USEPA.

Malady was aware that USEPA's procedures were the subject of debate in international forums. Their application to the case of 2,3,7,8-TCDD has been viewed as inappropriate and overly conservative by several respected scientists. However, other equally respected scientists have argued that, given the state of knowledge about carcinogenic mechanisms, in general, and 2,3,7,8-TCDD's mode of action, in particular, a more conservative approach is warranted. In support of their position, these latter scientists point to the ability of 2,3,7,8-TCDD to disrupt the reproductive process in animals, including monkeys. They note that at daily doses somewhat above one billionth of a gram per kilogram of body weight these animals suffered ill effects; e.g., spontaneous abortion and/or reduced fertility.

The Professor, now suffering more from the heat of the mind than the heat of the day, felt an increased need/desire for that beguiling glass of water. He resisted the urge, however,

knowing that he was already half way through his risk assessment. Only two more aspects called for consideration. The third step, Exposure Assessment, required an answer to the question: "How much 2,3,7,8-TCDD would I be exposed to by drinking this water?" To answer the question, the Professor could take the word of the notewriter that the concentration of 2,3,7,8-TCDD in the roughly 500 ml of water was 1 ppt; which is equivalent to a total mass of 500 picograms or 0.0000000005 grams, an amount that would be unnoticed by the human eye. Ingested into his slight 50 kg frame, 500 picograms would represent a dose of 10 pg/kg of bodyweight; indeed, a tiny dose in the minds of most people. In fact, the amount was so small that he nearly yielded to the impulse to reach out and drink the entire glass of water as a vivid demonstration of the absurdity of the idea that such a small amount could pose a meaningful risk to anyone.

[For a moment, the Professor considered sending a sample of the water over to his colleague Dr. Squint in the Chemistry Department of who it had been truthfully said: "If Squint can't analyze it, nobody can." In a moment, however, Professor Malady thought better about bringing Squint into the case. He recalled that sophisticated methods used in the analysis of 2,3,7,8-TCDD, called "gas chromatography/mass spectroscopy", were time-consuming and quite expensive. Malady decided that he was not that rich nor that thirsty!]

Malady's mind outwrestled his hand just as it was about to embrace the sparkling glass. For his mind knew that there was one more step -- one more question -- remaining in his risk

assessment: "What is the possible consequence of drinking this amount of water with this amount of 2,3,7,8-TCDD in it?" To answer this final question, the Professor reviewed in his mind

- a. All that was known and unknown about the toxic properties of 2,3,7,8-TCDD (Hazard Assessment): a wide range of toxic effects seen in animals at very low doses; limited, demonstrable toxicity seen in humans.
- b. All that was known and unknown about the potency of the 2,3,7,8-TCDD as a toxicant (Dose-Response Assessment): USEPA's and others' assessments of 2,3,7,8-TCDD as a uniquely potent carcinogen and a very potent reproductive toxicant.
- c. All that was known and unknown about the amount of 2,3,7,8-TCDD in the glass (Exposure Assessment): an unsubstantiated statement by an unknown notewriter. Keeping this mix of data, data gaps, informed opinion, and conservative assumptions in mind, Malady picked up his pencil, pulled his pad of writing paper to him, and carefully compared the alleged exposure with the dose-response assessments. He found that:
 - a. According to the USEPA analysis, if he were to drink a similar "2,3,7,8-TCDD cocktail" everyday of his 70 year life (that is, consume a daily dose of 10 pg of 2,3,7,8-TCDD per kg of body weight), the maximum chance that he would develop cancer as a consequence of this exposure would be about one in a thousand (10-3). The minimum chance could approach zero. [The USEPA approach

is not readily adapted to considering one-time exposures of the type in question here, but the one-time exposure risk would likely be considerably less than the lifetime continual exposure risk quoted here.]

b. According to the alternative analysis, if he happened to be in the critical stage of pregnancy (a thought which caused the Professor's face to flush in spite of himself), just this one glass of water would subject the good Doctor to a level of 2,3,7,8-TCDD (10 pg/kg) at or above the level deemed appropriate for humans; cf., 1 -10 pg/kg, in several European countries.

Professor Malady set his pad and pencil aside, leaned back in his chair, streched out his legs, and touching the fingertips of his hands together beneath his lips, contemplated the still still glass of water. His risk assessment -- as crude as it was -- was complete. He had the answers to the questions he asked. After all of this work he was now left with another question, a question of "risk management" this time, instead of "risk assessment"; namely "Knowing what I know now, should I drink the water?"

In many ways, this is the same question that confronted Malady at the start of his exercise just a few minutes before. But now he was armed with the results of the "scientific" portion of his decisionmaking process, and he could view his options from a more informed perspective. Now he had to balance what he knew about the risks of drinking the water against the non-risk

aspects of the decision; e.g., how thirsty he was; the proximity of other water sources; the example he would be setting for others; and the likelihood that other water sources were less contaminated with 2,3,7,8-TCDD or other pollutants.

Professor Malady remained in his attitude of contemplation/prayer, mulling these and other aspects over in his mind. After several minutes, he stirred, the concentration on his face relaxed into the hint of a knowing smile. Having made his risk assessment/risk management decision, he leaned forward in his chair, and ...

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RECENT INTERNATIONAL COOPERATION IN EXCHANGE OF INFORMATION ON DIOXINS

The subject of "dioxin" has become a topic of international conversation. During the past decade and a half, nearly every country in the developed world has confronted the environmental presence of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and its structurally related chemicals -- chlorinated dibenzo-p-dioxins (CDDs) and chlorinated dibeznofurans (CDFs). Sources of concern have included dumpsites, combustion sources, and contaminated chemicals.

The nations of Western Europe were at the forefront in determining the presence of CDDs/CDFs in the emissions associated with the combustion of municipal waste. Italy, Germany, and England were among the early sites of industrial accidents that led to the direct contamination of humans. The United States had the dubious distinction of being among the first to deal with widespread, low-level environmental contamination through inappropriate disposal of hazardous waste.

Through each of these incidents, and many others, the countries of the world have experienced and investigated major aspects of the problems associated with CDDs/CDFs. It is clear that we have much to gain by sharing our experience/information so that the sad learning-by-accidents and the important research

for solutions need not be repeated in each individual country.

For the past five years, thanks in large measure to the endeavors of Dr. Otto Huttzinger of the University of Bayreuth in Germany, scientists, government officials and members of the public have gathered yearly at the International Symposium on Chlorinated Dioxins and Related Compounds. These annual gatherings on alternating sides of the Atlantic Ocean have done much to advance our scientific understanding of the CDD/CDF problem and its possible solutions. Next year, for the first time, the Symposium will be hosted by our colleagues in Japan, further extending the international basis of these meetings. The network of expertise which has evolved from these meetings has provided an important, informal avenue for exchange of information.

During the past year, it has become clear that the pace of CDD/CDF related work is increasing and that important decisions and policies are being debated and formulated in different countries. For example, Canada, Germany, and The Netherlands are establishing "standards" for the allowable amounts of CDDs/CDFs in different situations. Sweden has invoked a moratorium on the construction of some municipal waste combustion units, while other countries have consciously encouraged construction of such facilities as a needed alternative to land disposal. It is important that the bases for these sometimes ostensibly different decisions be thoroughly understood by all parties. This understand can best be gained through face-to-face, collegial interactions.

In addition, there are benefits to be gained by exchanging hard-won scientific information on these compounds. For example, the United States Federal government has expended in excess of \$150 million over the past five years on 2,3,7,8-TCDD alone. This work has included extensive laboratory studies and several important epidemiological investigations, the major one of which will continue into the next century. The world's collective knowledge of the CDD/CDF problem can expand more rapidly, and its limited research funds be expended more efficiently if there is an effective exchange on both research planning and results.

With this background in mind, the Committee on Challenges of Modern Society (CCMS) of the North Atlantic Treaty Organization (NATO) has established a pilot project to facilitate the exchange of information on dioxins between countries. The leadership of the CCMS committee consists of three "co-pilots", each with a different area of primary responsibility: Germany (Technology Assessment); Italy (Management of Environmental Accidents); and the United States (Exposure and Hazard Assessment). Any NATO member country is free to participate in any or all of the groups. In addition, Austria, Japan, Sweden, and Switzerland, because of their interest and expertise in the area, have been invited to join in the exchanges. Other organizations have also been invited to participate: WHO, UNEP, OECD and CEC. In order to complete the array of interested parties, representatives of industry and environmental groups are welcome to participate as observers.

The first meeting of the CCMS group was in Bayreuth, Germany, immediately following the 5th International Symposium in September, 1985. The next full meeting of the group is scheduled for the fall of 1986. In the interim, each of the three subcommittees plans to conduct a separate meeting to exchange information. In addition, each country is submitting information to a central point about its on-going and planned research projects in the area of CDDs/CDFs for the foreseeable future. This information will be collated and distributed to the participating countries so that cooperative approaches will be facilitated and duplicative research avoided.

Some fundamental scientific questions await consensus resolution. For example, do the toxic properties of 2,3,7,8-TCDD exhibit thresholds, as viewed by some countries, or should the chemical be regarded as posing some finite risk, no matter how low the exposure might be, as viewed by some others? Also, what is the extent of CDDs/CDFs in human tissue throughout the world, what is its source, and what is its significance?

While basic scientific work proceeds apace to resolve these and other important questions, technological and regulatory concerns also need to be addressed. For example, what are some environmentally sound and effective ways of decontaminating CDD/CDF contaminated areas once they are found? How can we respond to environmental emergencies, such as a release of CDD/CDF, in an effective and efficient manner?

The problems posed by CCDs/CDFs are not likely to disappear soon. However, the NATO CCMS committee provides a

mechanism for maximizing our mutual efforts so that their combined impact will be more rapid and more forceful than they would be if they were pursued separately.

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CHLORACNE AND THE AGENT ORANGE PROBLEM IN THE U.S.A. VIETNAM VETERANS

INTRODUCTION

In this talk I am giving my personal opinion and assertions and these are not to be construed as official or as reflecting the views of the Veterans Administration (VA).

Dott. B. M. Shepard regrets he was unable to be here. He would have talked about Federal Research Projects in progress at this time: the soft tissue sarcoma studies; the mortality studies; an analysis of suicides among Vietnam Veterans; the U. S. Environmental Protection Agency (EPA) adipose tissue studies for levels of dioxin and Communicable Disease Center (CDC) studies. Instead, I would like to tell you about the area where I work with the Chloracne Task Force, and that is the Agent Orange problem among United States Vietnam veterans.

2. VIETNAM CONFLICT AND THE AGENT ORANGE PROBLEM

During the Vietnam conflict it was decided to defoliate 30 meters on either side of the highways to prevent ambush by the enemy. The phenoxyacetic acid herbicides had been used in the U.S. and around the world in agriculture and forestry work for twenty years with no serious health effects, so it was decided to use a 50:50 mixture of the 2,4,5-Trichlorophenoxyacetic acid (2,4,5-T) and 2,4-dichlorophenoxyacetic acid (2,4-D) in South Vietnam to spray the jungles: leaves died in one or two weeks and fell in about two months. In that thick jungle Tschirley estimated that only 6% of the herbicide actually reached the ground (1). Agent Orange (as it was called because it was transported in 55 gallon drums with a bright orange band) was found later to be contaminated by the highly toxic 2,3,7,8- tetrachlorodibenzo-p-dioxin (TCDD); this is a byproduct of production. From inventory samples it's known that 2,3,7,8-TCDD was present in 47 p.p.m. in early supplies and 2 p.p.m. during the conflict (2). It is estimated that 368 lbs. of TCDD was distributed

in the jungle of South Vietnam between 1965 and 1971. At that time, spraying was discontinued as the South Vietnamese were reporting birth defects and other health effects while U.S. animal researchers were reporting wasting syndromes, birth defects and liver tumors (3).

In 1970, the U.S. veterans became increasingly alarmed that the health effects and birth defects in their children might be due to their exposure to Agent Orange in South Vietnam. So the President created an Agent Orange Policy Group, the Veterans Administration set up an Agent Orange Projects Office and an Agent Orange Registry. Any veteran throughout the country who felt he had a health problem from Agent Orange, could go to his nearest Veterans Administration Hospital and give a history of his exposure and have a complete physical examination. If he had a skin problem he would be referred to dermatology.

3. DIOXIN PROBLEM AND VETERANS ADMINISTRATION

In the meantime, in Europe and in America chemical analyses for dioxin had become more sensitive and 2,3,7,8-TCDD had been found in high levels in fish, and lower levels in contaminated rivers and lakes, in municipal incinerators, in flue gases and fly ash, in beef livers, in cow's milk and in mother's milk. Fat levels in humans in the U.S., Canada and Europe are at about 7-10 nanograms per Kg. body weight. At the 5th International Symposium on Chlorinated Dioxins in Bayreuth, West Germany, September 16-21, 1985, Dott. Schecter looked at the levels in nine North Vietnamese and found no detectable TCDD, while in people from South Vietnam, the mean was about 22 p.p.t.(4) So what do these levels mean in humans? Most investigators agree that the most sensitive and specific marker of toxic absorption of dioxin in a human is a skin con-

dition: chloracne. Without chloracne no other toxic effects occur (5,6). If therefore the health problems of the U.S. veterans are due to Agent Orange these veterans would have to have chloracne. The Chloracne Task Force appreciated that chloracne is a rare occupational disease and few of the V.A. physicians had ever seen it. Therefore, the first thing that we did was to set up diagnostic criteria which were sent to the 172 Veterans Administration Hospitals in the U.S. The chloracne diagnostic criteria are listed in table I and were divided into four sections:

- 1) Essential (to make a diagnosis) 2) Compatible Histology

3) Acute Toxicity

4) Chronic Toxicity

The diagnostic criteria for chloracne following exposure to dioxin are: (1) exposure to chloracnegens (2) onset or aggravation of acne within a few weeks to two months, rarely later (average one month after exposure) (3) acne with predominance of large open comedones characteristically with strawcolored cysts (no cysts in mild cases) (4) atypical distribution such as the malar crescent of the face, crow's foot area lateral to eyes and in and behind the ears (5) history of 1 thru 4 and scars in distribution of 4 or 4 and 6 (6) severe acne with 3 and 4, plus inflammatory lesions, cysts and abscesses, on the face, ears, behind ears, back, buttocks, scrotum, outer upper arms, chest and thighs (7) compatible histology: comedones with thickened epithelial lining, few P. acnes, squamous metaplasia of outer root sheaths of hairs and sebaceous glands, keratin-filled cysts.

The criteria 1 through 5 are essential to diagnosis and are the most sensitive specific markers for dioxin toxicity.

4. COMMENT ON DIAGNOSTIC CRITERIA

TABLE I

VETERANS ADMINISTRATION CHLORACNE TASK FORCE CRITERIA FOR DIAGNOSIS OF CHLORACNE 2° to 2,3,7,8-TCDD EXPOSURE

ESSENTIAL

- 1. Exposure to chloracnegens
- 2. Onset or aggravation of acne within a few weeks to two months, rarely later (average one month after exposure)
- 3. Acne with predominance of large open comedones characteristically with
- straw-colored cysts (no cysts in mild cases)
 4. Atypical distribution such as the malar crescent of the face, crow's foot area lateral to eyes and in and behind the ears
- 5. History of 1 thru 4 and scars in distribution of 4 or 4 and 6 below
- 6. Severe acne with 3 and 4, plus inflammatory lesions, cysts and abscesses, on the face, ears, behind ears, back, buttocks, scrotum, outer upper arms, chest and thighs. This may occur but is not essential to diagnosis.

COMPATIBLE HISTOLOGY

- 7. Comedones with thickened epithelial lining, few P.* acnes, squamous metaplasia of outer root sheaths of hairs and sebaceous glands, minimal or absent sebaceous glands, keratin-filled cysts.
- 8. Onset preceding or coincident with acne of
 - (1) nausea, vomiting, nose bleed, diarrhea, blood in urine
 - (2) headache, fatigue, irritability, insomnia, impotence, loss of libido (delayed onset of these symptoms years later is not an effect of dioxin)
 - (3) lower leg pains, numbness
 - (4) tingling and/or numbness in fingers and toes
 (5) elevated liver enzymes
 (6) bursitis, edema arms and legs

 - (7) weight loss(8) triglyceridemia

CHRONIC TOXICITY

- (9) chronic bronchitis, decreased vital capacity(10) hypertrichosis on temples, hyperpigmentation of the face, no porphyrins
- (11) porphyria cutanea tarda (PCT) with porphyrins in urine and/or stool
- (12) peripheral neuropathy
- * P. = Propionibacterium

1.Exposure to Chloracnegens

The subject must be exposed to a chloracnegen (aromatic chlorinated hydrocarbon compound) in order to develop chloracne. The substances which cause chloracne are: 1) Polychloronaphthalenes (PCN) 2) Polybromonaphthalenes (PBN) 3) Polychlorobiphenyls (PCBs) 4) Polybromobiphenyls (PBBs) 5) Polychlorodibenzofurans (PCDF) 6) Polybromodibenzofurans (PBDF) 7) 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) 8) others: 1,2,3,4-Tetrachlorobenzene, Dichlobenil (Casoran)-a herbicide, DDT (crude trichlorobenzene). The one in which the Veterans Administration is interested is 2,3,7,8,-TCDD, the contaminant in Agent Orange.

2.Onset of acne usually one month after exposure.

Some of the veterans developed their skin problems three years or more after they came back from Vietnam; these problems cannot be due to Agent Orange Exposure in Vietnam; such a long latent period is never seen.

3. Large open comedones and straw colored cysts are prominent.

(During this session Ms. Fischmann has shown about 20 slides of clinical cases indicating: 1) large open blackheads; 2) small white cysts; 3) dark blue-grey noses; 4) blue fingernails and toenails.

4. Atypical distribution is characteristic.

Such atypical distribution is either not seen or less prominent in acne vulgaris.

5. History of chloracne and scars in atypical distribution.

It had been previously believed that chloracne cleared within a few years of cessation of exposure. However, in 1984 Suskind reported a 30 year follow-up on the industrial accident in Nitro, West Virginia (7). An unexpected finding was persistence of chloracne in 55.7% of the workers initially involved (8). It followed that chloracne, if initiated in Vietnam after exposure to Agent Orange, could be present in 55.7% of those afflicted.

Severe acne with acute inflammation.

This may occur but is not essential to diagnosis. This severe form may be confused with cystic acne.

7.Compatible histology

There are very few bacteria because herbicide kills bacteria.

During the conflict, no cases of chloracne had been reported. We have looked very carefully among the veterans using the CTF diagnostic criteria and have found 13 cases of chloracne and the majority of these were in engineering corps.

The first case of chloracne was in a veteran who had been in Vietnam for one year in an engineering corps with no trouble on the skin. He was transferred to a special unit to clear highways. The unit travelled in trucks and camped along the roads without going back to base. One team with bulldozers would put all the dead foliage in a big pile and then another team would come from behind and burn it. So they would get exposed to smoke, which has a much higher concentration of dioxin. They lived very intimately with the soil, they just dug out holes and lived in those, so they must have been breathing in the soil (Fig.1). Dott. Young has said that it takes a few weeks after contam-

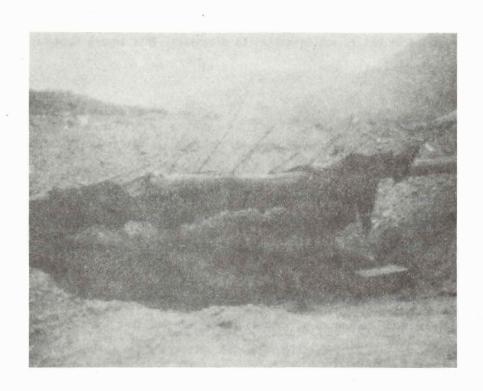


Fig.1 Shelter dug out of Agent Orange sprayed soil. Veterans living in intimate contact with 2,3,7,8-TCDD contaminated soil.

ination for dioxin to be irreversably bound to the soil so, probably, they had been getting dioxin breathing in smoke and dust and/or eating contaminated food (9).

This veteran, a few weeks after he began his job of clearing roads developed very marked blackheads in the deep creases on the sides of his neck. This is known to occur on skin after chemical exposures. Shortly after he had many pale cysts, blackheads and abscesses on his cheeks, on and behind his ears, back and buttocks. He also had the characteristic clear nose of chloracne (10). In Vietnam his skin problem was diagnosed as cystic acne. In addition, during the acute onset of chloracne, he had headaches, nausea and vomiting, which ceased shortly after removal from exposure.

One veteran, in addition to chloracne, has chronic lesions on his leg. We biopsied that area and noticed that there were some atypical lymphocytes in the infiltrate of a chronic dermatitis. So we are watching it very carefully because there have been some reports in the U. S. and other countries (Report from Sweden not yet confirmed) of soft tissue sarcomas and lymphomas (11,12).

CONCLUSIONS:

It is not known at what blood or tissue level chloracne occurs. The concentration of dioxin in Agent Orange in Vietnam was very low (2 p.p.m.) which explains why chloracne was neither described nor seen in Vietnam during the conflict. Some cases of chloracne were diagnosed in Vietnam as cystic acne and other acnes. Some of the soil in the Missouri horse arenas, where dioxin contaminated salvage oil was sprayed to keep down dust, had concentrations of dioxin as high as 31.8 to 33 ug TCDD per gm. (ppm) (2). So perhaps the con-

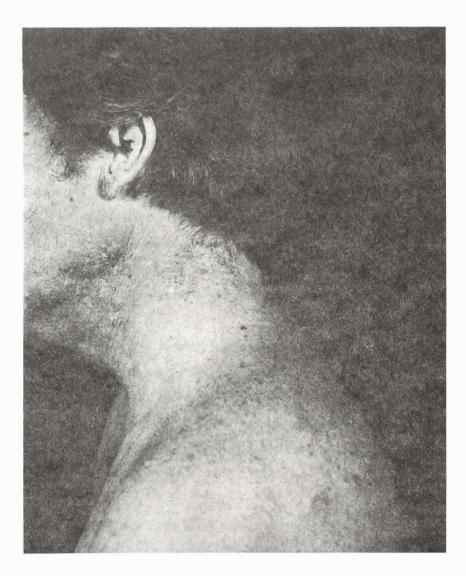


Fig.2 First U.S. Vietnam veteran with chloracne. Seventeen years after exposure to 2,3,7,8-TCDD from Agent Orange sprayed soil, comedones and striking, extensive, 1 to 2 mm pale cysts in neck creases, on and behind ears, shoulders and back are still present. Diagnosis in Vietnam: severe cystic acne vulgaris.

centration in Vietnam was too low to create toxic problems except in a few special instances, where the veterans were contaminated from soil and smoke. The studies on the pilots and technicians who flew on the spraying missions show no major health adverse effects in the veterans (13) and the birth defects study shows no major problems (14). So it would seem that there have been very rare cases of toxicity effects in U.S. veterans, only thirteen veterans with chloracne among the 33,512 studied. It requires further data to know if cancer will be a problem. The significance of the body burden that we all carry today is not known.

REFERENCES

- Tschirley, F. H. Response of tropical and subtropical woody plants to chemical treatments. Research Report CR-13-67. Agricultural Research Services, U.S. Department of Agriculture, Washington, D.C. p. 197, 1968.
- 2. Young, A.L., Calcagni, J.A., Thalken C.E., Tremblay J.W., The Toxicology, environmental fate, and human risk of herbicide orange and its associated dioxin USAF OEHL-78-92, USAF Occupational and Environmental Health Laboratory, 1978.
- Schwetz, B.A., Norris, J.M., Sparschu, G.L., Rowe, V.K., Gehring, P.J., Emerson, and C.G. Gerbig, Toxicology of Chlorinated Dibenzo-p-dioxins, Environ Health Perspect. 5:37-39, 1973.
- 4. 5th International Symposium on Chlorinated Dioxins in Bayreuth, West Germany, September 16-17, 1985, Chemosphere in press.
- 5. Crow, K.D., Chloracne Seminars in Dermatology 1: No. 4, 305-314, 1982.
- 6. Taylor, James S. Environmental Chloracne: Update and Review, Annals of the New York Academy of Sciences 320, 295-307, 1979.
- 7. Suskind, R.R. Chloracne and Associated Health Problems in the Manufacture of 2,4,5-T, Report to the Joint Conference, National Institute of Environmental Health Science, International Agency for Research on Cancer Lyon, France, January 11, 1978.
- 8. Suskind, R.R., Hertzberg V.S. Human Health Effects of 2,4,5-T and its toxic contaminants, JAMA, vol 251, no. 18, May 1984.
- 9. Young, A.L. personal communication.
- 10.Plewig G. and Kligman AM, Acne:morphogenesis and treatment, NY, Springer-Verlag, 1975.
- 11 Hardell,L. Sandstrom A. Case-control study: Soft-tissue sarcomas and exposure to phenoxyacetic acids and chlorophenols. Br J Cancer; 232;228-230, 1979.
- 12.Hardell, L. et al., Malignant lymphoma and exposure to chemicals especially organic solvents, chlorophenols and phenoxy acids: A case-control study. Br J. Cancer 43:169-176, 1981.
- 13.Lathrop, G.D., Moynahan, P.M. Albanese R.A. and Wolfe, W.H., An epidemiologic investigation of health effects in Air Force personnel following exposure to herbicides; Baseline morbidity results. Brooks Air Force Base, Texas: USAF School of Aerospace Medicine, Aerospace Medical Division, 1984.
- 14.Erickson, J.D., et al.: Vietnam veterans' risks for fathering babies with birth defects. JAMA 252: 903-912, Aug. 17, 1984.