

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

BEFORE THE ADMINISTRATOR

MAR 2 1980

In re:

The Dow Chemical Company, et al.

) FIFRA Docket Nos. 415, et al.
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DIRECT TESTIMONY OF MR. RONALD THOMAS */

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*/ This is the first of two documents containing Mr. Thomas' direct testimony. A portion of Mr. Thomas' testimony contains data which Dow claims to be confidential. This testimony is presented in a second document which has been filed UNDER SEAL for use in camera, and served only on the Administrative Law Judge, the Hearing Clerk, and the Dow Chemical Company.

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DIRECT TESTIMONY OF MR. RONALD THOMAS

INTRODUCTION

. My name is Ronald Thomas. I am currently employed as a supervisory chemist in the Residue & Special Projects Unit, Chemistry Section, Chemical & Biological Investigations Branch, Benefits & Field Studies Division, Office of Pesticide Programs, Environmental Protection Agency. Since 1956 I have been employed as an analytical chemist by federal regulatory agencies, namely the Food and Drug Administration, the U.S. Department of Agriculture, and the Environmental Protection Agency. Much of my career as a chemist has been in the field of pesticide residue analysis, and I currently specialize in that field. My curriculum vitae with a list of some of my publications is attached to the end of this statement.

My testimony is intended to describe the presence of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in commercial samples of 2,4,5-T and silvex products. Based on the work

done in my own laboratory, EPA contract laboratories, and others, I have concluded that commercial 2,4,5-T and silvex products manufactured in the United States in 1977-78 routinely contain TCDD at levels in the 10-30 ppb range. Dow discovery documents demonstrate the presence of TCDD in some batches of 2,4,5-T at levels higher than 30 ppb during this time period.

HISTORICAL BACKGROUND

My laboratory is responsible for investigating and attempting to resolve various analytical problems for the Office of Pesticide Programs, including analysis of air, soil, water and commodity samples for pesticide residues, and evaluation or development of analytical methodologies for detection and quantification of pesticide residues. From 1970 to the present, we have been involved in the analysis of the dioxin content of pesticide products, including the analysis of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in 2,4,5-T and silvex products.

The work in my laboratory has entailed the clean-up of samples by chromatographic means and the use of gas chromatography (GC) and low-resolution mass spectrometry (MS) for dioxin detection.^{1/} The limit of detection for dioxin achieved by the equipment in my laboratory is 0.1 ppm, with a margin of error of approximately 20% in the determinations. Between 1970 and 1978, my laboratory screened several hundred pesticide products for dioxin content. Dioxin levels greater than 0.1 ppm

^{1/} A short discussion of the theoretical basis of mass spectrometry is provided in Appendix A.

were detected in pre-1975 samples; however, for pesticide products manufactured after 1975, we did not find any samples with a dioxin content exceeding 0.1 ppm (100 ppb). The work performed in my laboratory from 1970-1972 is detailed in a paper published in 1972 (Exhibit A).

In 1977-78, the methodology for dioxin detection improved, and equipment became available which allowed a limit of detection of 0.01 ppm (10 ppb) for low-resolution GS/MS. In 1978, the Office of Pesticide Programs (OPP) undertook a project to determine the levels of dioxin in technical grade pesticide products likely to contain TCDD, including 2,4,5-T and silvex. Since my laboratory did not have the equipment to detect dioxin below the 0.1 ppm level, OPP entered into a contract with Gulf South Research Institute (GSRI), which had the equipment and the technical expertise to detect dioxin at a 0.01 ppm limit of detection level. My laboratory conducted an on-going quality control program for the GSRI contract throughout the duration of the contract. In this capacity, we had the responsibility of advising the contractor on the appropriate methodology, techniques and reporting methods; transmitting coded pesticide samples and reference samples for analysis; reviewing the results of the analytical determinations (for the reference samples and duplicates of the samples) while the study was in progress to assure that quality control was maintained; and providing any needed assistance and advice for the project.

On the basis of this monitoring program, we were able to conclude with great assurance that the contract and the analytical work had been carried out in a proper scientific manner commensurate with the state of the art of low resolution dioxin analysis. The results of the study, which will be discussed in greater detail in my ensuing testimony, establish that TCDD is present in commercial technical grade 2,4,5-T and silvex manufactured from 1977-78 at levels ranging from 0.01-0.03 ppm (10-30 ppb).

GULF SOUTH RESEARCH INSTITUTE (GSRI) STUDY
ON TCDD LEVELS IN TECHNICAL GRADE
2,4,5-T AND SILVEX AT THE PPB LEVEL

In 1978-1979, Gulf South Research Institute (GSRI), New Orleans, Louisiana, analyzed technical grade 2,4,5-T and silvex for TCDD at the 10 ppb level under an EPA contract.^{2/} The project was carried out under the direction of Joseph G. Montalvo, Jr., James F. Ryan, III, and Roy Flagg; the EPA Project Officer for the contract was Patricia Ott, Environmental Fate Branch of the Hazard Evaluation Division. The quality control for the contract was monitored by the EPA Residue & Special Projects Unit, under my supervision. The samples for the analysis were procured by the Enforcement Division of the Environmental Protection Agency from the manufacturing plants of the major manufacturers of the pesticide products in 1977-1978;

^{2/} In addition to various 2,4,5-T and silvex products, the study included the analysis of 2,4,5-trichlorophenol, an organophosphate, and a chlorinated phenolic antiseptic for TCDD content.

all the samples under study were taken from production tanks, bins or drums. The samples were coded by EPA in order to keep the sample contents anonymous; decoding information was provided to the Gulf South Research Institute only after completion of the assays and reporting of the TCDD data.

GSRI used low resolution gas chromatography/mass spectrometry (GC/MS) to determine the total TCDD content in technical grade samples of 2,4,5-T, the isooctyl ester of 2,4,5-T, the butoxyethyl ester of 2,4,5-T, the butoxypropyl ester of silvex and the isooctyl ester of silvex. A copy of the final contract report submitted by GSRI is attached (Exhibit B). The analytical method which was used to determine the levels of TCDD in the pesticide samples is described in detail in Exhibit B.

In order to assess dioxin recovery, an aliquot of a standardized radioactive solution of ^{37}Cl -2,3,7,8-TCDD was added to each sample prior to the sample clean-up procedure. The samples were prepared for analysis by caustic potassium hydroxide saponification of the pesticide followed by extraction of the neutral TCDD into hexane. The hexane solution was cleaned-up by extracting several times with sodium hydroxide solution and sulfuric acid, and was then dried, concentrated and chromatographed on alumina. The eluate was concentrated under nitrogen for GC/MS analysis.

The total TCDD in the technical grade samples was determined by low resolution gas chromatography/mass spectrometry

using a Hewlett-Packard 5985 GC/MC in the electron ionization source configuration. The standard addition injection technique was used and selective ion monitoring at 320/322 m/e^{3/} was performed for all samples. Complete mass spectra over the 150-350 range were obtained for all samples which gave a positive selective ion monitoring (SIM) scan. Six qualitative criteria for TCDD detection were developed to delineate the likelihood of TCDD detection in the analytical measurement system; these criteria are summarized in Table I of Exhibit B. For positive TCDD detection the criteria included (1) a recovery of ³⁷Cl-TCDD between 50 and 120 percent, inclusive; (2) both 320 and 322 m/e peaks at the TCDD retention time region; (3) well-defined 320 and 322 m/e peaks whose retention time exactly equals that of TCDD standards; (4) a signal-to-noise ratio of at least 2.5 times background at m/e 322; (5) a ratio of 320/322 m/e peak areas in the proper isotopic proportion and (6) TCDD confirmation by molecular ion spectra. The confidence in the TCDD detection was highest if all six criteria were met, and decreased as fewer criteria were met.

Samples were processed in sets which included internal standards and EPA supplied quality controls.^{4/} When the recovery

^{3/} TCDD gives a characteristic 320/322 m/e ratio; the presence of the expected 320/322 ratio provides a strong indication of the presence of TCDD, if other necessary criteria are met.

^{4/} TCDD standards in benzene were supplied by Aubry Dupuy, Toxicant Analysis Center, EPA.

fell within the specified contract range of 50-120% for a given sample, a duplicate assay was not performed; in cases where the recovery fell outside the specified range, a duplicate assay on an aliquot of the extract was performed. Contract requirements were satisfied if the average of the two recovery values fell within the specified range. Where the average recovery fell outside the specification range for the two aliquots, the original sample was reextracted and assayed again. The submission of at least two coded duplicates by my laboratory for each sample assured that the TCDD determinations were each based on a minimum of two duplicate analyses.

The contract did not require GSRI to report detectable values that fell below 10 ppb. Thus, although the mean detection limit achieved by GSRI was 4.7 ± 3.7 ppb, any result below 10 ppb was reported as non-detectable. In some samples, however, the presence of TCDD was indicated at levels below 10 ppb even though these samples were reported as non-detectable for TCDD at the 10 ppb level. The results of the study are summarized in Table I.

TABLE I
SUMMARY OF GSRI STUDY

PESTICIDE	NO. OF SAMPLES	NO. OF SAMPLES (PERCENT)		
		POSITIVE	DOUBTFUL [*]	NON-DETECTABLE
2,4,5-T	3	1(33.3%)	1(33.3%)	1(33.3%)
butoxyethyl ester of 2,4,5-T	10	9(90%)	1(10%)	0
isooctyl ester of 2,4,5-T	3	0	3(100%)	0
butoxyethyl ester of silvex	7	6(86%)	1(14%)	0
isooctyl ester of silvex	1	1(100%)	0	0

^{*}/ A sample was judged doubtful if it did not meet all the six criteria for positive TCDD detection.

TCDD was detected at levels ranging from 10 to 30 ppb in 9 of the 10 samples of the butoxyethyl ester of 2,4,5-T, in 1 of the 3 samples of 2,4,5-T, and was not detectable in three samples of the isooctyl ester of 2,4,5-T. For the silvex samples, TCDD was detected in 6 of 7 samples of the butoxypropyl ester and in the one sample of the isooctyl ester of silvex at levels of 10-30 ppb.

The results of the GSRI study are consistent with studies on 2,4,5-T and its derivatives performed, using methods similar to those employed by GSRI, by Buser and Bosshardt in 1974 and by Dow (Ramstad, Mahle, and Matalon) in 1977. The

Buser and Bosshardt study, which describes a gas chromatographic method for TCDD determination in technical 2,4,5-T (with confirmation by mass spectrometry of samples with a TCDD content greater than 100 ppb) and a gas chromatography/mass spectrometry method for TCDD determination in a 2,4,5-T alkyl ester and a 2,4,5-T amine salt, is attached as Exhibit C. Table II contains a summary of the results of the Buser and Bosshardt study. The TCDD content of these 2,4,5-T products ranged from 2 ppb to approximately 2000 ppb (or 2 ppm).

TABLE II
SUMMARY OF BUSER AND BOSSHARDT STUDY

<u>Pesticide</u>	<u>No. of Samples</u> ^{a/}	<u>TCDD Content (ppb)</u>
2,4,5-T (obtained from a German manufacturer prior to 1971)	3	300-600
2,4,5-T (obtained from a German manufacturer after 1971)	4	40-80
2,4,5-T (obtained from an American manufacturer prior to 1971)	1	~ 2000
2,4,5-T (obtained from an American manufacturer after 1971)	1	2
2,4,5-T alkyl ester (obtained from commercial sources in Switzerland in June, 1973)	2	20-50
2,4,5-T amine salt (obtained from commercial sources in Switzerland in June, 1973)	3	20-70

a/ The paper does not specify the number of duplicate determinations performed.

The Dow study, which describes an automated adsorption chromatographic system for the clean-up of commercial samples of 2,4,5-T ester for TCDD analysis by gas chromatography/mass spectrometry, is detailed in Exhibit D. The results of this study are summarized in Table III. The TCDD content of these 2,4,5-T samples ranged from 8 ppb to 26 ppb.

TABLE III
SUMMARY OF DOW STUDY

<u>Pesticide</u>	<u>No. of Samples</u>	<u>TCDD Content (ppb)</u> ^{a/}
1-isobutoxy-2-propyl ester of 2,4,5-T	^{b/} 1	^{c/} 26
butoxypropyl ester of 2,4,5-T	^{d/} 1	8

^{a/} The detection limit for TCDD was 5 ppb.

^{b/} The isobutoxypropyl ester was analyzed 18 times.

^{c/} The standard deviation was + 2 ppb.

^{d/} The butoxypropyl ester sample was analyzed at least in duplicate.

Exhibit E details a Dow method for the determination of TCDD in 2,4,5-T and related materials which is typical of the current state of the art in dioxin analysis.

Appendix B contains a summary of confidential Dow documents obtained in discovery which report the presence of dioxin in commercial samples of 2,4,5-T and related products. Because Dow claims that this information is confidential, this testimony has been filed UNDER SEAL for use in camera.

APPENDIX A

Mass spectrometry is one of the most important tools available to the analytical chemist for the analysis, identification, and confirmation of organic compounds. Gas chromatography (GC) is often used in conjunction with mass spectrometry (MS) to achieve a separation of the components that contributes to the overall sensitivity of the analytical determination.^{1/}

There are many variations in the instrumentation of modern GC/MS equipment, but basically all GC/MS systems contain (1) an inlet system for the test substance; (2) an ion source which bombards the test substance to produce ion fragments; (3) a mass analyzer which accelerates the ions at rates which depend on the mass/charge (m/e) ratio for the individual ions; (4) a collector on which ions of different m/e values are individually focused; and (5) a data processing system which gathers the spectral information and prints this information out on request.

The two most widely used mass analyzers are (1) the magnetic analyzer, which usually achieves the acceleration of the ions by varying the magnetic field at a constant electric potential and (2) the quadrupole system, which depends on the oscillation of the ions at varying radio frequency levels in a constant electrostatic field to achieve different acceleration rates for the ions generated in the source.

^{1/} In gas chromatography, the components of a sample travel through a chromatographic column by means of a carrier gas with retention times that depend on the physical and chemical characteristics of the components, the type of column used, and the running conditions for the instrument.

The most widely used technique for producing fragments in mass spectrometry is electron impact ionization, which produces a mass spectrum that is distinctive for the compound undergoing ionization. In electron impact ionization mass spectrometry, a substance is bombarded with an electron beam (usually 70 electron volts) to produce positive ion fragments, sometimes including a "parent ion", which gives the exact molecular weight of the compound. The largest fragmentation peak in the spectrum is called the "base peak" and is assigned a value of 100%; the other peaks, including the parent peak, are usually given as percentages of the base peak. To identify and/or quantify the molecular species under investigation, the analytical determination focuses on the fragmentation pattern, i.e. the m/e peaks, the parent peak and its isotope contributions, and the intervals between the peaks, as well as the abundance of the m/e species in the spectrum. Of particular importance are the isotope contributions to the parent peak (P), which are represented by the $P + 1$ and $P + 2$ peaks; reference to tables allows the determination of the molecular formula for a test compound on the basis of the P, $P + 1$, and $P + 2$ peaks. Compounds containing halogens (chlorine, fluorine, bromine and iodine) display a very distinctive set of peaks representing the isotopic contribution of the heavy halogen isotopes; for each halogen containing species, these

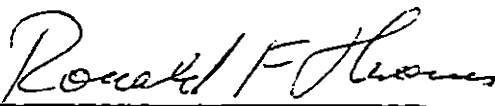
peaks appear in characteristic ratios which can be found in standard reference tables.^{2/}

The other prevalent method for generating ions is the chemical ionization method.^{3/} In chemical ionization mass spectrometry, electrons are used to ionize a reagent gas which subsequently reacts with the sample molecules to produce ions. Since the ions produced by chemical ionization have a much lower internal energy than those produced by electron impact ionization, chemical ionization mass spectra usually exhibit intense ions in the molecular weight region, while electron impact ionization spectra contain a preponderance of highly fragmented ions. Chemical ionization mass spectrometry has a comparable sensitivity to electron ionization mass spectrometry, as well as the advantage of allowing a choice of reagent gases to best achieve the characterization of the sample. The mass spectra obtained by chemical ionization are often quite different from those obtained using electron impact ionization. Sample preparation, which usually entails such procedures as solvent extraction and chromatography, is similar for the two methods.

^{2/} The most abundant ions in the electron impact ionization mass spectrum of TCDD are those of the molecular ion chlorine isotope cluster at m/e 320, 322, 324, and 326. The ions at m/e 320 and 322 are the most intense.

^{3/} In recent years, other methods such as field ionization and field desorption have received some attention, but these methods are not widely used.

For quantitative purposes, a technique known as selective ion monitoring (SIM) can be used to increase the sensitivity of the analytical determination. In this method, the instrument is set to detect only selected key ions, and a lower limit of detection is achieved for the ions of interest.



Ronald F. Thomas

EXHIBIT LIST

Exhibit A

Woolson, E.A., Thomas, R.F. and Ensor, P.D.J. 1972. Survey of Polychlorodibenzo-p-dioxin Content in Selected Pesticides. J. Ag. Fd. Chem. 20: 2.

Exhibit B

Monalvo, J.G., Ryan, J.F. and Flagg, R. Analysis of Technical Grade Pesticides for TCDD at the ppb Level. EPA Project No. 68-01-3981. Physical Engineering Sciences Division, Gulf South Research Institute, New Orleans, Louisiana.

Exhibit C

Buser, H. and Bosshardt, H. 1974. Determination of 2,3,7,8-TCDD at ppb Levels in Technical Grade 2,4,5-T in 2,4,5-T Alkylester and 2,4,5-T Amine Salt Herbicide Formulations by Quadrapole Massfragmentography. J. Chrom. 90: 71-77.

Exhibit D

Tore-Ramstad, Mahle, N.H. and Matalon, R. 1977. Automated Cleanup of Herbicides by Adsorption Chromatography for Determination of 2,3,7,8-TCDD. An. Chem. 49:

Exhibit E

Dow Chemical Company. Method ML-AM-75-34. Determination of TCDD in 2,4,5-T and Related Materials. Applicable to 2,4,5-T, Silvex and Chlorinated Phenols (unpublished).

Exhibit F

Documents which Dow claims contain confidential data on Dow's analysis of TCDD content in commercial 2,4,5-T produced between 1975 and 1979. (Filed Under Seal for use in in camera).

CERTIFICATE OF SERVICE

I hereby certify that copies of the foregoing
DIRECT TESTIMONY OF MR. RONALD THOMAS were hand delivered
or mailed first class postage prepaid on February 26,
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