Tetrachlorodibenzodioxin in the Environment: Sources, Fate, and Decontamination

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Introduction

Research on the behavior and fate of pesticides in the environment has provided a number of valuable techniques for assessing the impact of any organic substance intentionally or unintentionally released in the environment. These techniques can be applied to the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) to determine its behavior under comparable conditions. Important parameters affecting the environmental life history of any compound are movement, persistence, metabolism, plant uptake, translocation, photodecomposition, volatilization, and bioconcentration. Once these environmental properties are known about a compound, its anticipated behavior can be estimated, based on a comparison of information collected on registered pesticides. The modern registration process for pesticides entails a detailed accounting of the above mentioned parameters, plus information on efficacy and toxicology.

A second major consideration in assessing the impact of any organic substance in the environment is the total amount that may be present from current and past usage. For large-scale manufactured substances, production information is available if there are at least three manufacturers. Estimates on the occurrence of an impurity in any manufactured product may be extremely difficult to determine, unless this impurity has been recognized as a major contaminant and surveillance is implemented at an early stage of the production process.

Finally, once a substance has been identified as a potentially hazardous material, a safe, practical, and economically feasible decontamination process must be devised to use or destroy any known stocks.

The Agricultural Research Service became interested in the dioxin problem soon after the disclosure that it was associated with one of the older and widely used herbicides, 2,4,5-T [(2,4,5-trichlorophenoxy) acetic acid]. Our preliminary studies were directed toward identifying other sources of dioxins in pesticidal chemicals and learning something about the fate or life history of the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) in the environment. More recently time has been devoted toward helping in the assessment of decontamination methods that will successfully destroy TCDD. The present paper considers the sources, fate, and decontamination of TCDD in the environment.

Sources

Historically, TCDD has been associated with any process that uses 2,4,5-trichlorophenol as a starting material. A number of the currently used synthetic organic pesticides are derived from 2,4,5-trichlorophenol. In a survey of 17 pesticides examined for

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TCDD contamination, Woolson et al. (*1*) could detect TCDD only in older samples of 2,4,5-T and in one sample of silvex [2-(2,4, 5-trichlorophenoxy)propionic acid]. The level of contamination in the single sample of silvex was 1.4 ppm. Of 42 samples of 2,4, 5-T, 20 contained TCDD measured at a limit of sensitivity of 0.1 ppm. Of these 20 positive samples, 7 contained less than 10 ppm TCDD and 13 contained between 10 and 100 ppm TCDD. It appears, then, that TCDD contamination occurred primarily in samples of 2,4,5-T.

The United States production and domestic disappearance of 2,4,5-T for the years 1960–1970 are shown in Figure 1. The total production for this ten-year period was 106,-310,000 lb of 2,4,5-T expressed as the acid equivalent. The domestic disappearance figures for 2,4,5-T include military shipments abroad, primarily as defoliants for use in Vietnam. The peak year of production was 1968, when 17.5 million lb (about 16% of the ten-year total) was manufactured. Production sharply declined in 1969, to 5 million lb. The production figures for individual manufacturers are unavailable on a yearly basis. Although current data are lacking, older available data give some indication of the extent of use of 2,4,5-T. The total use of 2,4,5-T on farms, rights-of-way, and other nonfarm uses in 1964 was about 8,912,000 lb on 7,939,000 acres in the United States. The average rate of 2,4,5-T application on all domestic acreage in 1964 was about 1 lb/acre with a range from 0.25 to 2 lb/acre.

The best estimates on dioxin content in past samples of 2,4,5-T come from an extensive survey of approximately 15 million pounds of Herbicide Orange (200 samples) conducted by the U.S. Air Force (unpublished observations, 1973). Herbicide Orange is a defoilant containing about a 50/50 mixture of the butyl esters of 2,4,5-T and 2,4-D [(2,4-dichlorophenoxy) acetic acid]. The average dioxin content of the mixture was 1.91 ppm by weight (arithmetic mean) by use of a technique sensitive to 0.05 ppm. A frequency profile for these samples is shown in Figure 2. Of the 200 samples of Herbicide Orange, 136 or 68%, contained 0.5 ppm or less of TCDD. The highest sample contained 47 ppm TCDD. In the pesticide survey conducted by Woolson et al. (*1*) a 90% decline in TCDD was noted between 1968 and 1969 from one manufacturer. However, the level was still at 2–3 ppm in the 2,4,5-T acid. It is difficult and perhaps dangerous to extrapolate the total amount of dioxin added to the environment from previous use of 2,4,5-T for the following reasons: (1) from preliminary evidence available to us, it appears that different manufacturers produced 2,4-5-T with different TCDD contents over the

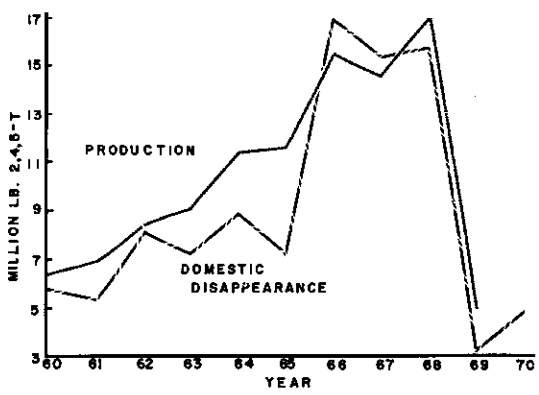

FIGURE 1. Production and domestic disappearance (includes military shipments) of 2,4,5-T acid in the U.S. (1960–1970).

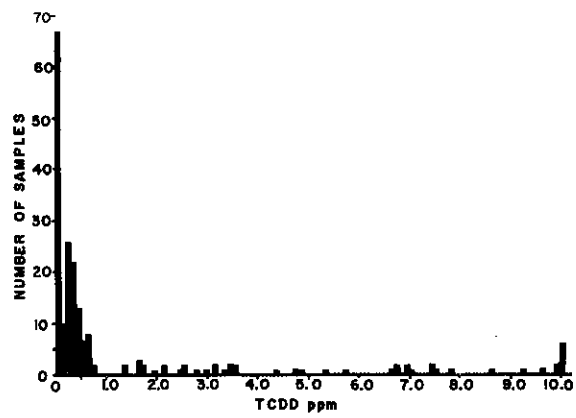

FIGURE 2. Distribution of TCDD content in 200 samples of Herbicide Orange. All samples containing more than 10 ppm appears as the last bar to the right of the figure.

10-year period, 1960–1969; (2) total production of each manufacturer and consequently the total dioxin content on a yearly basis is unknown, (3) it is difficult, if not impossible, in certain instances to attribute specific lots of 2,4,5-T to certain manufacturers; (4) the statistical significance of the inferences drawn from 200 samples is probably too small to reach any valid conclusion on a realistic input of TCDD from herbicide applications.

In 1971 when the dioxin issue first became known, we obtained and analyzed current production samples of 2,4,5-T acid then in production by the three principal manufacturers. They contained <0.1, 2.3, and 0.1 ppm.

By 1971, industry could provide commercial samples of 2,4,5-T that met the suggested limits of less than 0.5 ppm TCDD and could probably routinely produce 2,4,5-T with a TCDD content of about 0.1 ppm. Although we can make no statement about the past input of TCDD into the environment for the reasons stated above, some predictions can be advanced as to future input if the level of TCDD is held at 0.1 ppm in 2,4,5-T. If one assumes the 1964 usage of 2,4,5-T indicates the normal peace time usage, i.e., about 8 million lb applied at 1 lb pound per acre, then the amount of TCDD reaching the soil would be equal to 0.05 mg/acre. Assuming the surface 3 in. of soil weighs 1 million lb, the concentration would be 0.1 parts per trillion.

Fate in the Environment

A number of review articles covering various aspects of dioxin in the environment (*2, 3*) and in various environmental components including soils (*2, 4, 5*) sunlight (*6*), plants (*7*), and wildlife (*5*) have appeared from the USDA Pesticide Degradation Laboratory in Beltsville. A summary of these findings was presented in the review by Helling et al. (*8*) as follows.

TCDD was not photodecomposed on wet or dry soil surfaces nor was it produced photolytically from 2,4,5-trichlorophenol in water. TCDD is slowly lost in aqueous suspensions and in methanol.

Vertical movement of TCDD did not occur in a wide range of soil types. Contamination of underground water supplies seems very unlikely.

Approximately half of the TCDD applied at concentrations of 1, 10, and 100 ppm persisted in two moist soils after 1 yr under laboratory conditions.

Field applications of high rates (up to 942 lb/A) of 2,4,5-T on Lakeland sand produced no detectable (<1 ppb) TCDD residue when sampled 6 yr later to a depth of 1 m.

Soil metabolism of 2,4,5-trichlorophenol does not lead to the formation of TCDD as a condensation product.

Small quantities of TCDD (<40 ppb) were accumulated by young oats and soybeans grown on a sandy loam contaminated with TCDD (60 ppb). No TCDD was detected (<1 ppb) in mature plants or seeds grown on these same soils.

TCDD was not translocated from the point of application on the leaf surface to other plant parts. Some wash-off and possibly volatilization did occur.

Analyses of 19 eagle carcasses revealed no detectable (<50 ppb) dioxins. Admittedly more sensitive analytical techniques are needed before a clear picture of low TCDD wildlife levels can be assessed.

Because of its low solubility (3–5 ppb), relatively long persistence, lack of vertical mobility in soils, and inability to translocate in higher plants, TCDD more nearly resembles the shorter-lived chlorinated hydrocarbon insecticides in behavior than it does the more biodegradable phenoxyalkanoic acid herbicides, e.g., 2,4-D and 2,4,5-T.

Decontamination

Suspension of the use of Herbicide Orange in Vietnam has created large military surpluses that now must be used or destroyed. The U.S. Air Force has about 24 million lb of Herbicide Orange. Approximately 15 million lb contains an average of 1.91 ppm dioxin. Of the remaining material, which cannot be identified by manufacturer, approxi-

mately 80% contains less than 0.4 ppm dioxin. The political implications associated with Herbicide Orange may preclude its use as an herbicide, even though a substantial portion of the excess stock meets currently established EPA policy. Several conventional disposal methods, in addition to some new techniques, have been investigated to determine the safest, most economical, and most practical method for disposal of this material. Three options under consideration are incineration, soil biodegradation, and chlorinolysis. Since an environmental impact statement must be filed on the ultimate method or methods used for dealing with these surplus herbicides and their dioxin contaminate, several scientific investigations have addressed their efforts toward determining the parameters needed for successful destruction of TCDD.

Incineration appears to offer one of the safest methods for complete destruction of TCDD. In the present context incineration is defined as the high temperature reaction of TCDD with oxygen conducted in a unit equipped with proper emission control devices. By the use of differential thermal analysis, Kennedy and Stojanovic (Mississippi Agricultural and Forestry Experiment Station, personal communication, 1973) have estimated that temperatures of 800–1000°C will cause complete destruction of TCDD. These estimates are in good agreement with the value of 800°C published by Langer et al. (*9*).

Additional information is needed, however, on the composition of the stack gases and particulates, as well as water emanating from any industrial incineration process involving dioxins.

A second feasible method of dioxin disposal is soil biodegradation. Our work (*4*) indicates that approximately 50% of the added TCDD had been destroyed after 1 yr in soils at reasonably high concentrations. Woolson et al. (*5*) were unable to detect any TCDD in a Lakeland sand receiving approximately 1,000 lb of 2,4,5-T per acre over a 7-yr period. No TCDD could be detected at a minimum detection limit of <1.0 ppb in core samples to a depth of 6 ft. Although TCDD is fairly recalcitrant in soils, it is immobile and thus would offer no ground water contamination problems. Soil incorporation to a depth of about 6 in. seems to offer an additional advantage, i.e., it would prevent aerial movement on soil borne particles away from the site of application.

A third method of disposal of TCDD involves a new technology called chlorinolysis. This process involves the high temperature conversion of carbon compounds in pressurized atmosphere of chlorine to form carbon tetrachloride. In the United States, chlorinolysis is still in an experimental phase. We have cooperated with the Diamond Shamrock Company in pilot studies to investigate the stability of TCDD in samples of Herbicide Orange. A detailed examination of carbon tetrachloride produced from Herbicide Orange revealed no TCDD at a level of sensitivity of 10 parts per trillion, as measured by electron-capture gas chromatography. Chlorinolysis represents a major departure from conventional disposal systems in that it converts one product into another useful resource. In addition to carbon tetrachloride, phosgene and hydrochloric acids are products of chlorinolysis. Carbon tetrachloride has a major market in the production of freon, which has wide application as a coolant and propellant.

Summary

The major source of TCDD input in the past has been from use of the herbicide 2,4,5-T. Future inputs will be minimal if the dioxin content is held at low levels (0.1 ppm) during the manufacturing process.

In the environment, TCDD behavior is similar to some of the shorter-lived chlorinated hydrocarbon insecticides. It is fairly persistent and immobile in soils, not taken up into the economic portion of plants, and slowly decomposed in water in sunlight.

Several disposal options are available for the safe decontamination of surplus stocks of 2,4,5-T containing TCDD. These include incineration, soil disposal, and chlorinolysis.

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