

FATE OF DIOXINS IN SOIL: AN HISTORICAL OVERVIEW

A.L. Young

Office of Agricultural Biotechnology

U.S. Department of Agriculture

Washington, D.C. 20250

ABSTRACT

An historical overview of the fate in soil of the chlorodibenzo-p-dioxins (especially TCDD) is a story of the quest to measure "zero". With each new publication of findings of dioxin in the environment, more data were sought on how did it get there and whether the residue existed unchanged or as a derivative, a metabolite, or a complex in the environment. To answer each new question required more elaborate extraction techniques and more sophisticated instrumentation, and hence, fewer laboratories capable of doing the analysis. The ability to detect parts-per-trillion concentrations of dioxins in soil has forever changed the public's expectations of the detection levels required of the chemist, regardless of the compound in question. The ability represents a great accomplishment but a dangerous precedent!

INTRODUCTION

Perhaps no other class of chemicals has captured the attention and imagination of so many chemists and biologists as has the dibenzo-p-dioxins. The sources that have been identified [Hutzinger *et al.* (4)] are so numerous that the dioxins have been described as ubiquitous in our environment; yet, Czuczwa and Hites (3) have found that most environmental contamination is of recent origin (within the past 40 years). Thus it is not surprising that 20 years ago only a few chemists and even fewer biologists had any knowledge of dioxins. Yet in the brief time of two decades, the dioxins and related furans have had an extraordinarily significant impact on the advancements of methodologies and analytical instrumentation for the measurement of chemical contaminants in environmental substrates.

The early literature is characterized by inconsistencies and questionable explanations for data obtained from the analyses of soils for dioxins. It testified to the difficulty that was initially encountered in understanding the behavior of TCDD in the environment. It also indicated that new procedures for sampling, extracting, measuring and data handling were necessary for these unique compounds.

Beginning in 1970-71, when dioxin was found to be a contaminant of 2,4,5-T herbicide, numerous laboratories quickly evaluated the analysis by familiar techniques employed in their own laboratories (9). Microcoulometric GLC methods, thin-layer chromatographic procedures, infrared spectrophotometric methods and, eventually, gas chromatography with electron-capture detection systems were all employed. A number of laboratories employed multiple techniques for determining polychlorinated dioxins in a variety of substrates. In 1973, Woolson, Ensor and Young (7) reported on the analysis of soil and biological samples for TCDD. Samples that contained more than 1.0 ug/g of dioxin as determined by electron capture GLC were confirmed by the flame ionization detector, a microcoulometric detector, p values, ultraviolet irradiation, and/or gas chromatography-mass spectrometry. Although they used numerous techniques to cross-check their analyses, they reported that the minimum quantitative detection limit for TCDD was 0.5 ppm.

The major breakthrough on the analysis of dioxin occurred in a presentation by Baughman and Meselson at a Conference on Dibenzo dioxins and Dibenzofurans sponsored by the National Institute of Environmental Health Sciences, Research Triangle Park, N.C. in April 1973. They stunned the audience when they announced the development of a technique for reliably determining TCDD in environmental samples at levels approaching 1 ppt. Publication of their procedure occurred immediately afterward (2). The technique involved a very exhaustive cleanup procedure followed by preparative gas-liquid chromatography prior to quantitation. The purified TCDD extracts were sealed in capillary tubes for direct introduction into the mass spectrometer by an insertion probe.

Quantitation of TCDD at the part per trillion level was done by interfacing a Varian 1024 time-averaging computer with an Associated Electrical Industries MS-9 double focusing mass spectrometer.

The next major advancement in the analysis of environmental samples occurred as a result of the Seveso, Italy Dioxin Accident. Picchiari, Di Domenico et al. (5), and Balasso, Facchetti et al. (1) developed methods for routine analysis of hundred of soil samples at the ppt level. Meanwhile elaborate studies on sampling, movement, persistence and data handling were being conducted by Young and Cockerham (10), Yanders et al. (8), and Stalling et al. (6).

As Young (9) noted in 1980:

"The sophisticated instrumentation being brought on line for the determination of TCDD confirms the quest to measure "zero". Unfortunately even the lowest numbers obtained can be either pacifying or alarming, particularly when they may appear in the lay press without proper qualification. It must be remembered that it is not yet possible to prove the absence of a chemical. It is possible only to detect the presence of particular compound provided that our method is (1) sufficiently sensitive for the size of the sample, (2) that we have high purity standards available, and (3) that we collect a sufficient number of environmental samples to be statistically valid.

Perhaps when searching for such contaminants as TCDD, the best solution might be certification of the "absence" of harmful contaminants. This would mean that rather than having the residue analyst continue to search for ways to reach lower and lower limits of detection (and hence numbers that are more subject to human error and interpretation), the biologist should determine a threshold level at which no biological effects are noted. The chemist could then search for that "defined" level of no effect in the environmental substrate".

REFERENCES

1. Balasso, A., Fichtner, Girare, A. Leoni, C. Mauri and S. Facchetti. 1983. An efficient method for the quantitative determination of 2,3,7,8-TCDD at ppt level in soil samples. Chemosphere 12(4/5):499-502.

2. Baughman, R. W. and M. S. Meselson. 1973. An improved analysis for tetrachlorodibenzo-p-dioxins. *Adv. Chem. Ser.* 120:92-104.
3. Czuczwa, M. and R. A. Hites. 1985. Dioxins and Dibenzofurans in Air, Soil and Water. *IN:* Karmin, M. A. and P. W. Rodgers (Ed.). *Dioxins in the Environment*. Hemisphere Publishing Corporation, Washington. P: 85-99.
4. Hutzinger, O., M. V. Berg, K. Olie and S. Safe. 1985. Dioxins and Furans in the environment: evaluating toxicological risk from different sources by multi-criteria analysis. *IN:* Karmin, M. A. and P. W. Rodgers. *Dioxins in the Environment*. Hemisphere Publishing Corporation, Washington. P: 9-32.
5. Pocchiari, F., A. Di Domenico, V. Silano and G. Zapponi. 1983. Environmental impact of the accidental release of tetrachlorodibenzo-p-dioxin (TCDD) at Seveso (Italy). *IN:* Coulston, F. and F. Pocchiari. *Accident Exposure to Dioxins-Hum Health Aspects*. Academic Press, New York. P: 5-35.
6. Stalling, D. L., J. D. Petty, L. M. Smith and W. J. Dunn. 1985. Dioxins and Furans in the environment; a problem for chemometrics. *IN:* Karmin, M. A. and P. W. Rodgers. *Dioxins in the Environment*. Hemisphere Publishing Corporation, Washington. P: 101-126
7. Woolson, E. A., P. D. J. Ensor and A. L. Young. 1973. Dioxin residues in lakeland sand and bald eagle samples. *Adv. Chem. Ser.* 120:112-118.
8. Yanders, A. F., C. E. Orazio, R. K. Puri and S. Kapila. 1989. On translocation of 2,3,7,8-tetrachlorodibenzo-p-dioxin: time dependent analysis at the Times Beach Experimental sites. *Chemosphere* 19(1-6):129-432.
9. Young, A. L. 1980. Methods of detection and analysis. *IN:* R. W. Bovey and A. L. Young, *The Science of 2,4,5-T and Associated Phenoxy Herbicides*. John Wiley and Sons, New York. P: 239-300.
10. Young, A. L. and L. G. Cockerham. 1985. Fate of TCDD in field ecosystems - assessment and significance for human exposures. *IN:* Karmin, M. A. and P. W. Rodgers (Ed.). *Dioxins in the Environment*. Hemisphere Publishing Corporation, Washington. P: 153-171.