

Environmental Fate of TCDD and Agent Orange and Bioavailability to Troops in Vietnam

Nathan J. Karch¹, Deborah K. Watkins¹, Alvin L. Young², Michael E. Ginevan¹

¹Exponent, Inc., Washington, DC, USA

²University of Oklahoma, Norman, Oklahoma, USA

Introduction

This paper reviews the environmental fate of Agent Orange and the contaminant, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), and discusses how this affects the bioavailability of TCDD for ground troops in Vietnam.

Methods and Materials

From 1962 to 1971, herbicides were sprayed in Vietnam to defoliate the jungle canopy and to destroy crops, exposing the enemy and denying them food, and to clear tall grasses and bushes from the perimeters of US base camps and outlying fire-support bases. The most widely used herbicides were phenoxyacetic acids – 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), picloram and cacodylic acid. Only the herbicides containing 2,4,5-T were contaminated with TCDD – Agents Orange, Green, Pink and Purple.

Dispersion of Agent Orange: The US Air Force was responsible for training aircrews, developing aerial tactics for herbicide missions and the developing, testing and evaluating spray equipment. These programs were conducted mainly at Eglin Air Force Base, Florida and to a lesser degree at Pran Buri Calibration Grid in Thailand. Responsibility for the defoliant rested with the US Army at Fort Detrick, Maryland with the cooperation of the US Department of Agriculture.^{1,2}

Extensive field tests with herbicide determined optimum conditions and deposition rate for Vietnam. Dispersal of herbicide droplets by air turbulence could be minimized by scheduling missions in favorable weather conditions and by controlling droplet size. Agent Orange was found to be most effective in defoliating when applied to the target vegetation: while wind was calm (i.e., less than 8 knots), in the absence of precipitation, and early morning.^{1,3}

RANCH HAND missions achieved optimum defoliation by flying at 140 knots and an altitude of 50 meters above the ground level (just above tree tops). These parameters allowed the aircraft to be on target for 3.5-4 minutes and resulted in a particle size where 98% of the particles were greater than 100 microns, meaning they have a rapid settling velocity.⁴ Tests showed that 87% of the

herbicide would have impacted the vegetation within one minute and within the width of the swath. The remaining 13% of the herbicide took longer to settle (due to vortexes at the wing tips), drifted or was volatilized.⁵

The relatively small proportion of Agent Orange applied by other methods (5% of the total applied) posed less potential for drift than fixed wing application. Helicopters flew at much lower speeds and altitudes, and hand-held and truck spraying was effectively at zero speed and altitude. Thus, defoliation for helicopter and ground spraying operations were probably even more effective than for fixed wing applications.

The Forest Canopy and the Leaf Area Index: Forests have many layers of foliage structured to receive sunshine and convert it into energy. When gaps occur among leaves, the leaves tend to grow where the escaped sunlight will reach it. The amount of sunlight, rain, or herbicide that is intercepted by a forest canopy depends on the density of the vegetation. In a multi-canopy forest, such as in much of Vietnam, the topmost layer of the canopy receives the largest percentage and each canopy layer underneath intercepts a successively smaller portion.

Foliage density is quantified as a leaf area index. The leaf index is used for calculations involving photosynthesis, carbon absorption, and oxygen exchange and to define the amount of canopy penetration by light, rain, or herbicides. The leaf area index is quantitatively defined as the total leaf area in proportion to the ground surface below. For example, a leaf area index of 2.0 means that two square meters of leaves per square meter of ground surface.

More than half of Vietnam was double and triple canopy jungle, and most spraying missions were conducted over these jungles. Agent Orange was applied principally to forests with leaf index values ranging from 2 to 5. As the leaf area index increases, the proportion of applied herbicide intercepted by the foliage increases as well. In these dense forests, the target canopy target intercepted 70 – 90% of the herbicide sprayed. Vegetation below the canopy received 3 – 14% of the spray, with the higher percentage resulting in those areas where the forest is sparse. The underbrush or forest floor received about 1 – 6% of the total aerial spray.⁶

Photochemical Degradation of TCDD: Agent Orange would dry upon spraying within minutes and could not then be dislodged. TCDD would generally adhere to the organic plant surfaces, where light would destroy it within hours, or longer depending on the level of sunlight. A relatively small proportion might be absorbed into the plant before degradation, where it would become bound and biologically unavailable. Agent Orange that penetrated to the ground would be degraded by sunlight that reached the ground in roughly the same proportion. Any TCDD present would either be photodegraded at a rate comparable to the upper canopy or would quickly bind to forest litter or exposed soil, again rendering it biologically unavailable.

In the presence of sunlight, therefore, TCDD in Agent Orange was rapidly destroyed by photodegradation. Crosby and Wong (1977) found that when Agent Orange was spread on leaves and exposed to natural sunlight, the half-life of its TCDD content was less than six hours.⁷ They determined that the requirements for photodegradation of TCDD were: dissolution in a light-transmitting film or material; the presence of a hydrogen-donor (such as herbicide); and ultraviolet light. Jensen et al. (1983)⁸ found that TCDD levels in rangeland grasses following application of

DIOXIN IN VIETNAM: CHARACTERISATION, MONITORING, REMEDIATION AND EFFECTS

2,4,5-T herbicides decreased rapidly in outdoor sunlight. Bentson (1989)⁹ demonstrated the photodegradation of TCDD on a number of substrates and at a range of light intensities. His work shows that the decomposition of TCDD continues in reduced light at a reduced rate. Reduced light levels are present on cloudy days and in shade and generally contain the same wavelengths as direct sunlight at roughly equally reduced intensities, including, in particular, the ultraviolet wavelengths that degrade TCDD.

Norris (1981)¹⁰ also confirmed the relatively rapid disappearance of TCDD from leaves even under low light conditions. A half-life of 7 to 10 hours was observed when the ultraviolet light was set low light conditions. He found that photodegradation continued even in the absence of a hydrogen-donor, with more than 90% of TCDD degraded after seven days of exposure to ultraviolet light, showing that water vapor can serve as a hydrogen donor.

Because herbicide spray missions were scheduled in the early morning on days when there was no precipitation, the applications of Agent Orange typically were followed by hours of sunlight. Since liquid Agent Orange itself transmits ultraviolet light and is an excellent hydrogen-donor, as is water and water vapor which are present in abundance in the jungle, photodegradation of TCDD in Agent Orange would have proceeded rapidly in Vietnam and would have occurred even the relatively shady forest understory, albeit at a slower rate.¹⁰

Penetration to Soil: Almost all Agent Orange was intercepted in the forest canopy or photodegraded on plant and ground surfaces, and a very small percentage penetrated the canopy and reached soil. In contrast to its rapid photodegradation in sunlight, TCDD in the absence of herbicide contamination (which supports microbial degradation) is persistent and immobile once bound to soil. If some TCDD in soil becomes exposed to ultraviolet light, such as in surface soil or soil being tilled or otherwise disturbed, the TCDD will degrade by photolysis. Since a person is most likely to encounter surface soil, it would tend to have negligible TCDD levels when sunlight reaches the surface soil. In addition, the principal manner of movement of TCDD in soil is by volatilization, and as it volatilizes at the surface it photodegrades.¹¹

Several studies were conducted on TCDD in soil on the spray-equipment testing grids at Eglin AFB. In one report, Young (1983) concluded that photodegradation during and immediately after application destroyed nearly all of the TCDD in herbicides applied on the test site (99.9%).¹² However, once below the soil surface, the low residues of TCDD (in the absence of herbicide) remained confined in the top 15 centimeters of soil 14 years following application of 37,000 kilograms of 2,4,5-T.¹³ In Agent Orange storage sites at the Naval Construction Battalion Center, and at Johnston Island, long-term monitoring studies of TCDD in soil were conducted. These studies showed that the persistence of TCDD in the top 8 centimeters at spill sites had a half-life less than two years.¹⁴ These sites had high levels of herbicide and increased microbial populations, confirming the role of microbial degradation of TCDD in the presence of herbicide.¹³ A significant consequence of the strong binding to soil is that TCDD is not leached from the soil by rainfall into surrounding areas. TCDD is virtually insoluble in water.

Typically, TCDD is not detectable in streams or ditches adjacent to areas in the US where 2,4,5-T was used repeatedly.^{15, 16} TCDD can be briefly present in surface water bound to floating particles of soil.¹⁶ However, TCDD would be exposed to sunlight near the surface of the water and degrade

DIOXIN IN VIETNAM: CHARACTERISATION, MONITORING, REMEDIATION AND EFFECTS

within a few hours or days^{7, 17, 18, 19} TCDD also volatilizes from rivers and ponds, with half-lives (of dissipation from water surfaces) of approximately 6 and 32 days, respectively. Once volatilized, TCDD photodegrades very rapidly in the atmosphere, with a half-life of less than an hour.¹⁸ As a result of TCDD's lack of solubility in water and strong binding to soil, surface water is not a source of substantial exposure to TCDD.

Skin Absorption: Newton and Norris (1981)²⁰ investigated the rate of skin absorption of a 2,4,5-T herbicide containing dioxin by applying the herbicide to 900 cm² areas of skin on volunteers. The concentrations applied were representative of commercial applications at the time, ranging from 2.4 to 38.4 g/l of acid equivalent 2,4,5-T as an ester emulsified in water. After two hours of saturated contact with a large area of bare skin, only 0.15 to 0.46 percent of the 2,4,5-T penetrated the skin, entered the body, and was eliminated in the urine. Applications of the highest concentrations of 2,4,5-T resulted in the lowest proportion of 2,4,5-T absorption. Although TCDD was not measured penetrating the skin directly, there is other evidence suggesting that TCDD penetrates with about the same proportion as observed with 2,4,5-T.²¹

Results and Discussion:

The prospect of exposure to Agent Orange in ground troops in Vietnam seems unlikely in light of the environmental fate of TCDD and the herbicides in circumstances likely to have occurred in Vietnam. Photochemical degradation of TCDD and the limited bioavailability of any residual TCDD present in soil or on vegetation lead to the expectation that dioxin levels in ground troops who served in Vietnam would be low or indistinguishable from background levels. Most veterans who served in Vietnam were likely to have only limited opportunities for contact with Agent Orange. Agent Orange was applied as droplets averaging approximately 0.3 millimeters in diameter that dry very quickly.

A very narrow window of time – typically a few minutes – was available after spraying before drying. The amount of TCDD actually absorbed due to a single exposure is extremely small, and the amount of herbicide in a single exposure is unlikely to affect the level of TCDD in the body. Once Agent Orange and TCDD dried on plant surfaces and the TCDD became bound, it is unlikely that to have become bioavailable thereafter. The TCDD degraded in sunlight quickly, even in low levels of light, and would be gone in a matter of days. If bound to soil out of the sunlight, it was not readily bioavailable and was poorly absorbed. If it was adsorbed onto woody plant tissue sufficiently that sunlight was blocked, it was not bioavailable.

The Centers for Disease Control (1988)²² reported that serum analysis of TCDD in over six hundred veterans judged likely to have been exposed to Agent Orange in Vietnam had the same serum TCDD levels as veterans who never served in Vietnam. Levels of TCDD did not increase with greater likelihood of exposure based upon military records or upon self reported exposure. This failure to distinguish serum TCDD levels in ground troops with the highest potential for exposure highlights that exposure reconstructions based upon analysis of military records are poor predictors of actual absorbed dose.

To absorb dioxin from Agent Orange, direct skin contact with liquid Agent Orange is necessary. Vietnam veterans who had elevated serum levels of TCDD came in contact with the liquid

herbicide²² and were involved aerial spraying as part of the RANCH HAND operation or were in the Chemical Corps who also handled Agent Orange in Vietnam.^{23, 24,25}

Conclusion

The evidence from an evaluation of the environmental fate and bioavailability of TCDD from Agent Orange is consistent with the observation of little or no exposure in the vast majority of Vietnam veterans. Appreciable exposure requires repeated long-term contact of the type experienced by RANCH HAND and Chemical Corps veterans who handled or otherwise had direct contact with liquid herbicide.

References

1. Buckingham WA (1982): The Air Force and Herbicides in Southeast Asia 1961-1971. Office of Air Force History, United States Air Force, Washington, DC.
2. Bovey RW, Young AL (Eds) (1980). The Science of 2,4,5-T and Associated Phenoxy Herbicides. Wiley-Interscience Publications, New York, NY.
3. Cecil PF (1986). Herbicidal Warfare: The RANCH HAND Project in Vietnam. Praeger Special Studies, Praeger Scientific, New York, NY.
4. Young AL, Calcagni, JA, Thalken, CE, Tremblay, JW. (1978). The Toxicology, Environmental Fate, and Human Risk of Herbicide Orange and its Associated Dioxin. USAF OEHL TR-78-92, USAF Occupational and Environmental Health Laboratory, Brooks AFB, TX.
5. Harrigan ET (1970): Calibration Test of the UC-123K/A/A45Y-1 Spray System. Technical Report ADTC-TR-70-36, Armament Development and Test Center, Eglin AFB, FL.
6. Klein RE, Harrigan ET (1969): Comparison Tests of Defoliants. Technical Report ADTC-TR-69-30, Armament Development and Test Center, Eglin, AFB, FL.
7. Crosby DG, Wong AS (1977): Environmental Degradation of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD). *Science* 195: 1337-1338.
8. Jensen DJ, Getzendaner ME, Hummel, RA, Turley J (1983): Residue Studies for 2,4,5-Trichlorophenoxy Acetic Acid and 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin in Grass and Rice. *J Agric Food Chem* 31: 118-122.
9. Bentson, KP (1989): Short-term Fate of Xenobiotic Substances in Pesticide Deposits. Ph.D. Thesis. College of Forestry, Oregon State University
10. Norris LA (1981): The Movement, Persistence, and Fate of Phenoxy Herbicide and TCDD in the Forest. *Residue Reviews* 80: 66-135.
11. Freeman RA, Schroy JM (1989): Comparison of the Rate of TCDD Transport at Times Beach and at Eglin AFB. *Chemosphere* 18 (1-6): 1305-1312.
12. Young AL (1983): Long-Term Studies on the Persistence and Movement of TCDD in a Natural Ecosystem. *Environ Sci Res* 26: 173-190.
13. Young AL, Cairney WJ, Thalken CE (1983): Persistence, Movement and Decontamination Studies of TCDD in Storage Sites Massively Contaminated with Phenoxy Herbicides. *Chemosphere* 12 (4/5): 713-716.
14. Young AL, Thalken, CE, Ward WE (1975): Studies of the Ecological Impact of Repetitive Aerial Applications of Herbicides on the Ecosystem of Test Area C-52 A, Eglin, AFB, FL. Technical Report AFATL-TR-75-142, Air Force Armament Laboratory, Eglin AFB, FL.

DIOXIN IN VIETNAM: CHARACTERISATION, MONITORING, REMEDIATION AND EFFECTS

15. Norris LA (1996): Degradation of 2,4-D and 2,4,5-T in Forest Litter. *J Forestry* pp. 475-477.
16. Matsumura FA, Benezet HJ (1973): Studies on the Bioaccumulation and Microbial Degradation of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin. *Environ Health Perspect* 81: 253-258.
17. Crosby DG, Wong AS (1973): Photodecomposition of 2,4,5-Trichlorophenoxyacetic Acid (2,4,5-T) in Water. *J Agric Food Chem* 21: 1052-1054.
18. Podell RT, Jaber HM, Mill T (1986). Tetrachlorodibenzodioxin: Rates of Volatilization and Photolysis in the Environment. *Environ Sci Tech* 20(5): 490-492.
19. Plimmer, JR (1978): Photolysis of TCDD and trifluralin on silica and soil. *Bull. Environ. Contam. Toxicol.* 20(1): 87-92.
20. Newton M, Norris, LA (1981): Potential Exposure of Humans to 2,4,5-T and TCDD in the Oregon Coast Range. *Fund Appl Toxicol* 1: 339-346.
21. Weber LW, Zesch A, Rozman K (1991): Penetration, Distribution and Kinetics of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin in human skin *In Vitro*. *Arch Toxicol.* 65: 421-428.
22. The Centers for Disease Control and Prevention (CDC) (1988): Serum 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin in US Army Vietnam-era Veterans. *JAMA* 260(9): 1249-1254.
23. The Air Force Health Study – Final Report (2000), Chapter 2. Dioxin Assay. Prepared by SAIC for the Air Force Research Laboratory, Brooks AFB, TX
24. Michalek JE, Akhtar FZ, Ketchum NS, Jackson WG (2001). The Air Force Health Study: A Summary of Results. *Organohalogen Compounds* 54: 396-399.
25. Kang HK, Dalager NA, Needham LL, Patterson DG, Matanoski GM, Lees PS (2001): Health Status of US Army Chemical Corps Vietnam Era Veterans Relative to Current Serum Dioxin Concentration. *Organohalogen Compounds* 54: 392-395.