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DISPOSAL OF HERBICIDE ORANGE
BY SOIL BIODEGRADATION

10 June 1972

A REPORT OF FINDINGS AND RECOMMENDATIONS

BY

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NOTE: This is a report prepared by the investigator for limited circulation. The views and recommendations expressed by the author are his own and do not represent the policies nor commit support from the United States Air Force Academy Command.

ABSTRACT

The Air Force is charged with responsibility for ecologically safe disposal of approximately 2.3 million gallons of herbicide Orange. This report provides information on the feasibility of using a soil incorporation technique for the biological (microbial) degradation of the herbicide. Research data have shown that massive amounts of 2,4-D and 2,4,5-T (the components of Orange) can be biologically destroyed by microorganisms. Moreover, data substantiate biological degradation of the toxic contaminant dioxin (TCDD). Data confirm that such large quantities of herbicide can be biologically degraded within an acceptable time frame (1 1/2 years). Special details are provided on the soil incorporation technique and on the criteria for the selection of a suitable site for the disposal program.

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SECTION I: INTRODUCTION

The Air Force is charged with responsibility for ecologically safe disposal of approximately 2.3 million gallons of herbicide Orange. Initially, high temperature incineration by CONUS commercial operators was proposed. However, there have been adverse reactions on the part of certain state environment agencies which may preclude this course of action. This report is designed to provide information on an alternate disposal method; namely, the biological degradation of the herbicide by a soil incorporation technique. The disposal of herbicide Orange by soil degradation should be considered for the following reasons:

(1) soil incorporation has definite cost advantages; an estimate of \$300,000 is proposed; (2) soil incorporation provides a relatively fast technique for the disposal of such a large quantity of agent; a time estimate of 240 days is proposed; (3) soil incorporation in a carefully selected site will provide an ecologically safe disposal; degradation data are available on all components of herbicide Orange including the contaminant 2,3,7,8-tetrachlorodibenzo-p-dioxin; (4) properly employed this technique will minimize manpower requirements, the proposal calls for a 10-man operation to include soil incorporation of the agent and drum cleaning and disposal; (5) soil incorporation offers an alternate

disposal method for those areas where incinerators are not available; and (6) this method may provide a reasonable socio-political solution if the factors in Section VII are given serious consideration.

The rationale for the soil incorporation technique is based on pertinent literature and field studies. It has been known for several years that the rate at which herbicides disappear from the soil is largely dependent upon their susceptibility to metabolism by soil microorganisms. Much of the information available on the biological breakdown of the components of Orange, 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), comes from laboratory studies and is very useful for predicting what might happen when relatively high concentrations of 2,4-D and 2,4,5-T are applied to a soil incorporated site. Conversely, a certain amount of caution must always be used when extrapolating laboratory data to a field situation.

Until recently there was very little information concerning the breakdown of 2,4-D or 2,4,5-T in a soil incorporation site. However, Dr. R. L. Goulding (Environmental Health Sciences Center, Oregon State University, Corvallis, Oregon, Phone 503-754-2814) is presently conducting field experiments on the use of soil incorporation as a method for disposing of massive quantities (approximately 1 1/4 million gallons) of 2,4-D and waste by-products. A copy of Dr. Goulding's January 1972 progress report is attached. Of significance, Dr. Goulding found that when he employed a trenching technique, simulating subsurface injection, he could place 500 pounds/acre (1b/A) 2,4-D at a depth of 10 inches into 5-inch bands on two-foot centers. With this placement the actual concentration of material within these bands was

approximately 1250 parts per million (ppm). Samples taken between trenches and in soil profile segments from the surface down through the point of application indicated minimal vertical and horizontal movement of the agent from the site of initial deposition. Results from this experiment indicated little difference in the rates of degradation in the trenched plots or a surface application of 500 lb/A: 95% degradation in 540 days.

Data obtained on soil persistence of large quantities of 2,4-D and 2,4,5-T are also available from the Eglin AFB one square mile spray equipment test grid that was used from 1962 to September 1970 (50). This area was sprayed with approximately 21,265 gallons of Orange and 16,164 gallons of Purple (also a 2,4-D and 2,4,5-T formulation) during a seven-year period (1962-1969). The area also received 4,172 gallons of White (2,4-D and picloram herbicide) between 1967-1970. In May 1970, plant bioassays indicated that the maximum concentration of 2,4-D and/or 2,4,5-T in the soil was 5 ppm. If all of the 2,4-D and 2,4,5-T from the military herbicides had remained in the top six inches of the soil and had not decomposed during the eight-year period, then the approximate concentration would have been 1,550 ppm combination of 2,4-D and 2,4,5-T. In December 1970, the maximum detectable level of a combination of 2,4-D and 2,4,5-T in the soil was 0.1 ppm. Chemical analysis of soils collected in December 1970 indicated that no dioxin could be detected at a minimum detection limit of 0.001 ppm dioxin (49).

SECTION II: AGENT DESCRIPTION

Orange is a reddish brown to tan-colored liquid soluble in diesel fuel and organic solvents, but insoluble in water. One gallon of Orange contains 4.21 pounds of the active ingredient of 2,4-D and 4.41 pounds of the active ingredient of 2,4,5-T. Orange is formulated to contain a 50:50 mixture of the n-butyl esters of 2,4-D and 2,4,5-T. The percentages of the formulation are:

n-butyl ester of 2,4-D	49.40%
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)	0.62%

Some of the physical, chemical, and toxicological properties of Orange are:

Specific density (25 C)	1.282
Viscosity, centipoise (23 C)	43
Molecular mass	618
Weight of formulation lbs/gal	8.63
Soluble in water	No
Relative toxicity	Low
Specific toxicity for white rats (mg/kg)	566

Orange and its component n-butyl esters of 2,4-D and 2,4,5-T are characterized by plant physiologists as volatile herbicides because the vapors are relatively phytotoxic. However, the physical chemist would

regard the butyl esters of 2,4-D and 2,4,5-T as essentially nonvolatile, with a vapor pressure of less than 1 mm of mercury at 35 C. In fact, the n-butyl ester of 2,4-D is approximately equivalent to No. 2 diesel fuel in volatility, requiring a temperature of 147 C for vapor pressure to equal 1 mm of mercury (20).

Data are not available on the distance Orange or its component esters may travel in vapor state from sprayed areas, but lateral movements of herbicides, due to their volatile nature along, are believed to be negligible. Most instances of alleged crop damage adjacent to areas sprayed with Orange may be attributed to drift or misapplication at the time of spraying rather than to volatility (20). Perhaps the most appropriate data on the potential of Orange to effect damage to agronomically important plants downwind from application comes again from research (unpublished data, Captain Young) on dissemination studies of Orange on Test Area C-52A, Eglin AFB Reservation, Florida. The large quantity of herbicides (57,000 gallons), deposited aerially, and the possibility of drift (and/or volatility?) fostered several monitoring systems for possible environmental contamination. Strategic placement downwind of sensitive indicator plants (tomato and cotton) at distances of 0.5, 1.0, and 2.5 miles indicated essentially no damage was done to the plants positioned at 2.5 miles, while only light and moderate damage (galling and tissue enlargement) occurred to those positioned at 1.0 and 0.5 miles, respectively.

The dioxin formation was the cause for concern over the use of Orange. 2,4,5-trichlorophenol is employed in the manufacture of 2,4,5-T. It can condense to form 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). This compound is extremely toxic and elicits teratogenic effects (See Section V). In a

personal communication with Mr. Wayne E. Vandeventer (SAAMA/SFQT, Kelly AFB, Texas, Autovon 945-5613), data were obtained on the dioxin content of the Orange currently stored at Gulfport, Mississippi. From an analysis of 18 drums the range of dioxin content was 0.1 to 14.0 ppm. Approximately 50% of the drums contained dioxin content within the limits set by the Environmental Protection Agency (0.5 ppm dioxin). The average dioxin content of the drums was calculated to be 3.3 ppm.

SECTION III: CURRENT USES OF PHENOXY HERBICIDES

The phenoxy herbicides 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) are well established pesticides for the control of weeds and shrubs in agriculture. In particular, as noted by Klingman and Shaw (27), the phenoxy herbicides are especially useful because: (a) they are selective; they kill most broadleaf plants but do not kill grasses or grain crops; (b) they are potent; many species of weeds are controlled by less than one pound of active ingredient per acre; (c) they are easy to use; (d) they are not poisonous to man, domestic animals, or game when applied at the recommended rates; and (e) they do not accumulate in the soil and they have no harmful effects on soil organisms. Klingman and Shaw noted that ester formulations are generally more potent, pound for pound, than are salt formulations. The esters are more effective than salts for killing weeds that are growing slowly; and because esters are oily, they are less likely to be washed off the foliage if rain falls soon after application.

The herbicides 2,4-D and 2,4,5-T were first employed by farmers and ranchers in the mid-1940's and remain the most common synthetic organic herbicides. They are used in several situations. The largest use of 2,4-D is for broadleaf weed control in corn and other grains; the major use of 2,4,5-T is to kill brush (14). The combined production of 2,4-D and 2,4,5-T has increased steadily from 34.6 million pounds in 1958 to 96.8 million pounds in 1968. At present, the phenoxy herbicides are the only group of herbicides used to any extent on pasture and rangeland. Weeds and brush infesting pasture and rangeland are most widely controlled

by 2,4-D and 2,4,5-T, respectively. In 1966, nearly 8 million acres (more than 1 percent) of pasture and rangeland were treated with phenoxy herbicides (14). The herbicide 2,4,5-T is a particularly effective tool for vegetation management on forest lands (33). It is used on powerline, railroad, and road rights-of-way; but its most important use is in connection with the establishment and release of conifers on forest lands. For these purposes, 0.5 to 4 pounds of 2,4,5-T per acre are applied as low volatile esters dissolved or emulsified in diesel oil or water.

The 15 April 1970 government edict on 2,4,5-T suspended the registrations of liquid formulations for use around the home and recreational areas, and for uses on lakes, ponds, and ditchbanks. This restriction did not include its use on range and pasture lands, non-agricultural lands, or in weed and brush control programs on communication and highway rights-of-way.

SECTION IV: LITERATURE REVIEW

The interrelationships of soil microorganisms and herbicides are observed in two areas of study: (a) effects of herbicides on microorganisms and (b) effects of microorganisms on herbicides. The first area relates to the effects by direct or indirect action of the herbicide on the growth and physiological processes of the soil microflora. The second area of study deals with the metabolism and breakdown of herbicides into components that are usually less phytotoxic than the original compound.

There is considerable evidence available to show that 2,4-D as contained in Orange is rapidly decomposed in soils (2). Concentrations of 2,4-D at 100 to 200 times the amounts normally used for Weed control usually have no appreciable effect on the soil population of bacteria, fungi, and actinomycetes (36). Reduced bacterial counts have been observed with 2,4-D concentrations as low as 100 ppm, but in several experiments 500 ppm have not altered bacterial counts. More is known about the effects of 2,4-D on soil microflora than about any other herbicide, and some interesting interactions have been observed (36). The herbicide is more toxic to microorganisms in acid than in alkaline soils and most toxic to aerobes and facultative anaerobes. Spore-forming bacteria appear to be more sensitive than nonspore-formers to 2,4-D. Bacteria are more sensitive than fungi to the herbicide. Even closely related species differ in response to 2,4-D.

If 2,4-D were applied to a moist loam soil under summertime temperature at a rate of 0.5 to 3 lb/A, it would disappear in 7 to 30 days (26). If applied at rates of 4 to 55 lb/A, it would probably disappear in one to three months (12). If 2,4-D were applied to the soil at a concentra-

tion of 500 ppm (1,000 lb/A) and disappeared at a rate proportional to the breakdown of 55 lb/A, the calculated time is 5.6 years. However, there is evidence that a more realistic time for inactivation of 500 ppm would be one to two years or maybe less.

Soil microorganisms have remarkable adaptive power and several people have shown that microorganisms can, through adaptation or mutation, alter their metabolic pathways for a more efficient utilization of herbicides (5). When microorganisms are exposed to high concentrations of a foreign material, there is usually a lag period before utilization of the material begins. This lag period represents the time required for the microorganism to become adapted. Once breakdown is initiated and completed the soil then retains a capability for rapid breakdown. For example, Audus (2) treated a soil with 100 ppm of 2,4-D and 20 days were required for 80% detoxification and when the soil was treated again only three days were required for 80% detoxification. Colmer (6) found that 5,000 ppm of 2,4-D was at first inhibitory to a bacterium, but after subculturing three times the organism grew rapidly in the 5,000 ppm concentration. Newman et al. (34) and Rogoff and Reed (40) discovered that 2,4-D disappeared from soil more rapidly with the second application. Walker and Newman (46) found in laboratory tests that three to five days were required for decomposition of 100 ppm, 2,4-D; but when the same soil was treated again with 1,000 ppm then only 10 to 14 days were required for decomposition. Stojanovic et al. (43) added a mixture of 2,4-D and 2,4,5-T (similar to the military formulation of Orange) to soil at a concentration of 5 tons/A (5,000 ppm in top 6 inches). Seventy-eight percent of the herbicide carbon was given off as CO₂ in 56 days. It

also appeared that mixtures of 2,4,5-T were more rapidly degraded than were the single compounds.

Persistence of 2,4,5-T in soils is usually two to three times longer than 2,4-D (12), and very few organisms have been identified as having the ability to break down the 2,4,5-T molecule (1). Dr. Michael Newton, Oregon State University, (35) has calculated from studies on the kinetics of degradation by microorganisms that 2,4,5-T has a half-life of 7 weeks in the forest floor. Dr. Newton also has noted (personal communication) that in tropical soils, a three gallon per acre application of Orange (27 pounds active ingredient/acre) disappeared within 10 days. He estimated the 2,4-D disappeared in 3 days and the 2,4,5-T in 10 days. Leopold, Van Schaik, and Neal (29) found that increasing chlorination of phenoxyacetic acid decreased its water solubility while increasing its absorption onto activated carbon and organic matter, thus making it less available for microbial degradation. Moreover, Thiels (44) noted, from reviewing the literature, that 2,4,5-T is less susceptible to attack by microorganisms because the aromatic nucleus of halogenated phenoxyalkyl carboxylic acids and phenols are more biologically inert in compounds containing the halogen (chlorine) in a position meta (the 5 position) to the phenolic hydroxy.

There are some microorganisms that are susceptible to phenoxy herbicides (2,4-D and 2,4,5-T) at concentrations of about 50 ppm (5). However, most microorganisms are resistant to high concentrations. Shennan and Fletcher (41) subjected 38 species of soil bacteria, fungi and actinomycetes to 2,4-D and 2,4,5-T at concentrations of 100 to 10,000 ppm. Twenty-six species were not inhibited by 10,000 ppm 2,4-D. Twenty-four organisms

required 10,000 ppm 2,4,5-T for growth restriction to occur. Stojanovic et al. (43) added a mixture of 2,4-D and 2,4,5-T to soil at a concentration of 5 tons/A and the bacteria and actinomycetes were inhibited but the total number of fungi increased during a 56-day incubation period.

It seems apparent from the literature that over the millennia, microorganisms have developed unbelievable capabilities for handling organic compounds. Moreover, most microorganisms seem to have a latent ability for decomposition of halogenated hydrocarbons. In a recent review, McNew (32) discussed the degradation of just such organic compounds in the soil. He noted that the degradation of such chemicals are dependent upon the enzymatic capabilities of the microorganisms. There are certain types of enzymes that destroy the molecules by hydrolysis at vulnerable spots such as an oxygen group or ester linkage, oxidation over an unsaturated bond or hydroxyl group, reduction, substitute reaction with a carboxyl or halogen substituent, or beta oxidation of an alkyl chain. McNew illustrates this degradation process by discussing the fate of 2,4-D in soil:

In normal loam soils rich in soil microorganisms there is hydrolysis to inactive acetic acid and 2,4-dichlorophenol within 2 to 6 weeks, depending upon the moisture and temperature of the soil. The acetic acid is immediately used as an energy source by entering into the Krebs cycle of almost any microorganism. The 2,4-dichlorophenol is further degraded by those organisms that attack phenols through the hydroxyl group. If instead of 2,4-D, an application is made of the inactive ester 2,4-dichlorophenoxyethanol sulfate, Bacillus cereus var. mycoides hydrolyzes off the sulfate group, certain species of Pseudomonas or other bacteria oxidize the resultant alcohol to an acid, thereby producing 2,4-D which then undergoes decomposition by the means described above. In substance, the soil microorganisms can be encouraged to generate the

herbicide in situ and then decompose it before excessive residues build up. This is an ideal self-regulant device but it has three drawbacks to discourage its general use: more chemical must be applied per acre, it can be ineffective on some soils with low microbial populations, and the system is extremely susceptible to variations in the environmental conditions.

The question can now be asked: "What are the breakdown products from phenoxy herbicides and do they accumulate in the soil?" Loos, Roberts, and Alexander (30), and Bollag et al. (3,4) have extensively studied in cultures the decomposition of 2,4-D by a soil Arthrobacter. They have suggested that the bacterium first enzymatically converts the 2,4-D to 2,4-dichlorophenol and other chlorophenols. These chlorophenols are further metabolized to catechols (e.g., 3,5-dichloro catechol and 4-chlorocatechol). At low enzyme levels, the chlorocatechols are metabolized completely. At high enzyme levels other compounds are apparently formed. Bollag et al. (3) have identified these as carboxymethylenebutenolides. The butenolides are probably converted to chloromuconic acid and then to chloride ion, acetate and dicarboxylic acid. They concluded by noting that the toxicity of many of these intermediates is unknown and inasmuch as they are found in cultures of a microorganism obtained from soil, they may accumulate during the decomposition of phenoxy herbicides. But do they actually accumulate under field conditions? Investigations by Winston and Ritty (48) and Reigner, Sopper, and Johnson (38) indicated that both 2,4-D and 2,4,5-T are decomposed to form carbon dioxide, inorganic chlorides, and water; objectionable chlorophenols are not end-products of this decomposition. Further supporting evidence has been provided by Reinhart (39). The

upper half of a 60-acre timber watershed in northern West Virginia was logged and treated with a 2,4,5-T ester to kill all vegetation. The volume of herbicide that was applied was 1,325 gallons on 30 acres (44 gallons/acre). Almost 800 gallons of this was potential contaminating material: about 740 gallons of diesel oil and 52 gallons of a commercial formulation of 2,4,5-T (312 pounds acid equivalent). Reinhart found no odor contaminants (phenols or catechols) in the numerous water samples taken from the stream draining the treated watershed.

The amount of active herbicide applied to soil may diminish by means other than biological decompositions; e.g., chemical degradation, absorption, metabolism by plants, volatilization, leaching, and photodecomposition.

Hanks (16) has shown that 2,4-D was much more resistant to leaching from alkali soil than from a peat soil. Hernandez and Warren (17) found that high organic matter content in the soil reduced the movement of 2,4-D by leaching.

Moreover, herbicides once applied to the soil surface are exposed to the forces of light, air heat, moisture, and other environmental influences. Such "weathering" acts, in some degree, to change the initial character of the herbicide. While each factor individually may cause chemical transformations, the influence of light appears to be the most important and widespread of all. The herbicides 2,4-D and 2,4,5-T undergo photodecomposition.

Crosby (9) has noted that while many of the herbicides are decomposed readily by ultraviolet light in the laboratory, data from field experiments

are not always in agreement. The atmosphere effectively absorbs ultraviolet light of short wave lengths; and the intensity of the light is strongly affected by season, climate, latitude, elevation, and the angle of incidence. Shading, however, is not as important a factor as might be suspected; the intensity of ultraviolet reflection from open sky often exceeds that from direct sunlight. Crosby and Tutass (10) compared the effects of sunlight and ultraviolet light on aqueous solutions of 2,4-D (440 ppm). The solutions were confined to a depth of 3.5 inches and a pH of 3.5. They found that 2,4-D decomposed rapidly in the presence of water and ultraviolet light. The major reaction in the laboratory was in the formation of 2,4-dichlorophenol. This was further degraded to a mixture of polyquinoid humic acids (a light-independent reaction). Sunlight appeared to produce many of the same qualitative effects as the ultraviolet light in the laboratory. However, 2,4-dichlorophenol was not detected in the sunlight. This was probably due to rapid volatilization under outdoor conditions. The fact that humic acid was found in the sunlight-irradiated mixture suggested that a significant part of the herbicide was degraded to this end-product.

Aly and Faust (1) examined the effects of ultraviolet irradiation (in the laboratory) on the isopropyl ester, butyl ester, and isooctyl ester of 2,4-D. They found that the irradiation by a mercury lamp decomposed the esters of 2,4-D at a rate which was pH dependent. Degradation occurred faster at pH 9.0 than at pH 7.0 or 4.0. These results appear to be in disagreement with the results of Crosby and

Tutass (10) primarily because of the differences in the 2,4-D formulations. The acid and salt formulations are soluble in an acid system while the ester formulations are not.

Since the solubility of a formulation is important, it should be recognized that the addition of an ester to an aquatic system (e.g., a pond) would probably result in the accumulation of the herbicide on the bottom and, hence, in the mud (recall that Orange has a density of 1.282). Frank and Comes (15) investigated the persistence of 2,4-D in pond water and the associated hydrosol (mud). They found that when the butoxyethanol ester of 2,4-D was added to ponds, it accumulated in the top one inch of the hydrosol. They also found that low concentrations of the 2,4-D persisted in the pond water for 25 days and in the hydrosol for 55 days.

Newton (35) reported that photochemical degradation was one of the most important mechanisms of 2,4,5-T loss in a forest ecosystem.

SECTION V: THE FATE OF DIOXIN (TCDD) IN THE ENVIRONMENT

In the latter part of 1969, it was revealed by the National Cancer Institute that a study (8) conducted by the Bionetics Research Laboratories, Division of Litton Industries, had shown 2,4,5-T at very high dosage levels to be teratogenic (producing malformed fetuses) in mice and rats. Subsequent studies (47) showed that a toxic contaminant, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) was responsible for most of the findings attributed to 2,4,5-T. The sample of 2,4,5-T employed in the Bionetics study contained 30 ppm TCDD.

Sparschu, Dunn, and Rowe (42) have noted that TCDD is highly toxic. The LD_{50} for male and female rats is 23 and 45 $\mu\text{g}/\text{kg}$ respectively, while that for male guinea-pigs is 0.6 $\mu\text{g}/\text{kg}$. They also noted that TCDD was responsible for human cases of chloracne (a disease clinically similar in all patients and characterized by a profuse acneiform eruption, starting on the face and extending to the trunk and limbs, appearing 3-9 weeks after contact with TCDD contaminated herbicide).

Additional studies (13) have shown that oral administration of 2,4,5-T containing ≤ 1 ppm TCDD produced no teratogenic effects in rats at doses as high as 24 mg/kg/day. Furthermore, New Zealand White rabbits receiving a daily oral dose of 40 mg 2,4,5-T/kg on days 6-18 of gestation showed no clinical or gross pathological signs of adverse chemical effect. Litter size, number of foetal resorption, birth weights and sex ratios appeared to be unaffected by the chemical treatment.

Williams (47), has stated that TCDD can be formed in the manufacture of 2,4,5-trichlorophenol, the precursor to 2,4,5-T. The conditions required for its formation are high temperatures in the presence of base, conditions which can occur in the alkaline hydrolysis of 1,2,4,5-tetrachlorobenzene to 2,4,5-trichlorophenol. No detectable dioxins have been found in 2,4-D. This is due to the fact that the precursor 2,4-dichlorophenol is made by direct chlorination of phenol and not by alkaline hydrolysis of 1,2,4-trichlorobenzene. To date, analytical methods have been developed and validated to a sensitivity of 0.1 ppm for TCDD in 2,4,5-T acid.

Johnson (22) has summarized some of the information known about TCDD: (a) in solution it is rapidly degraded by ultraviolet light at wavelengths that appear in the spectrum of the sun. (b) the tetrachloro-dibenzo-p-dioxin has one-fifth the solubility of DDT in water and one-sixteen hundredth the solubility of DDT in benzene. Thus, there is probably less tendency to concentrate in fat, but the question is really academic because the quantities of TCDD in the environment are exceedingly small. (c) speculative claims are widespread that 2,4,5-T residues on vegetation might be converted to TCDD if the dead foliage is burned. All available evidence to date indicates this conversion does not occur. The alleged precursor is in dilute form on the substrate, the reaction is bimolecular---the molecules must be formed close together to react. A laboratory experiment was conducted wherein agent Orange was applied to filter paper at a rate of 24 lb/A. This is equivalent to approximately 10 lb of 2,4,5-T acid equivalent per acre. The paper was

burned and combustion products plus ash was solvent extracted and analyzed by gas chromatography. There was no TCDD detected at a sensitivity of 5 ppm.

Environmental studies by Kearney et al. (24) indicate that TCDD is not biosynthesized by condensation of chlorophenols in soils, is not a photoproduct of 2,4,5-trichlorophenol, does not leach into the soil profile, is not taken up by plants from minute residues which might occur in soils, is not photodecomposed on a dry soil surface and is not translocated within the plant from foliar applications. TCDD could not be detected at a level of 0.05 ppm in tissue extract from 22 Bald Eagle carcasses. Examination of soil samples receiving heavy application of 2,4,5-T revealed no TCDD. It is concluded that environmental contamination by chlorodioxin impurities in 2,4,5-T have produced no measurable effects.

Dr. Phillip C. Kearney (Leader, Pesticide Investigation, USDA, ARS, Beltsville, Maryland, Phone: 301-474-6500, Ext. 370) has reported (personal communication) that TCDD is degraded by microorganisms! In studies of soils containing 0.1, 1.0, and 10 ppm TCDD, 50% degradation was noted within one year. The proposal contained in the present report (Section VI) is based on the addition of 500 ppm Orange to the soil (via soil incorporation). If all the Orange contained 14 ppm dioxin (which it does not), then the concentration of dioxin would be 0.007 ppm on a per acre basis and 0.035 ppm on a 5-inch band treatment pattern (see Section VI).

Little research has been devoted to the nature and toxicological significance of trace amounts of impurities in pesticide chemicals. However, the observation that samples of 2,4,5-T did contain small amounts of TCDD has led to an increased interest in the nature of impurities in other herbicides. Recently, Huston (19) has isolated and identified three neutral contaminants in samples of production grade 2,4-D. These impurities interfered with the gas-liquid chromatographic analysis of 2,4-D for TCDD. The compound bis-(2,4-dichlorophenoxy)-methane was present at a concentration of 30 ppm in commercial samples of 2,4-D. The other two compounds were positional isomers of the first and were present in much less concentration (1 and 10 ppm, respectively). The toxicological significance of these three compounds as impurities in production grade 2,4-D is not known. However (as Huston noted), from a study of the teratogenic effects of both production grade 2,4-D and purified 2,4-D, it appears that these impurities have no adverse effects at the levels administered in laboratory tests.

SECTION VI: RECOMMENDATIONS

From information provided in Sections I - V it is apparent that any technique for the disposal of 2.3 million gallons of Orange must most importantly be ecologically safe and economically feasible. To be ecologically safe means that the 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) must be destroyed in such a manner as to preclude any hazard to man, wildlife, or to the ecology of the disposal site. Obviously, it is not the 2,4-D or 2,4,5-T that presents the disposal problem. If the Orange contained less than 0.5 ppm TCDD, it could be declared surplus and sold. Because the Air Force has no way (i.e., without the actual analysis of each drum for TCDD) of identifying the significantly contaminated lots, it becomes necessary to destroy all the agent! Research data by Young, Hunter, and Lehn (50) at Eglin AFB, Florida, showed that massive amounts of 2,4-D and 2,4,5-T were biologically destroyed by micro-organisms in the soil. Moreover, Dr. Goulding's research in Oregon confirms that massive amounts of 2,4-D and other phenolic wastes can be biologically degraded within an acceptable time frame (1 1/2 years). Dr. Kearney's research at Beltsville, Maryland, confirms biological degradation of TCDD. Therefore, it is felt that biological disposal of Orange by soil incorporation is an excellent means for destroying the agent. Economically, it is the cheapest! Dr. Goulding's disposal program in Oregon has been tasked with the destruction of 1 1/4 million gallons of herbicide waste or approximately 25,000 drums. He estimates (personal communication) that the disposal project will cost \$60,000.00.

It is proposed that a subsurface injection system be used to incorporate

the herbicide into the soil at a depth of 6-10 inches. The injection could be done by using a D-8 CAT or similar heavy piece of equipment and utilizing a conventional agricultural subsoiler consisting of a vertical blade on which a chisel, or foot, is mounted at an angle of approximately 15° from horizontal. A piece of metal tubing should be attached to the blade (and terminating at the base of the chisel) in such a manner that a piece of hose from the injection pump could be inserted to permit deposition of the herbicide immediately behind the chisel. The equipment, with eight injectors (shanks), should be calibrated to apply 1,000 lb/A of Orange. The eight shanks should be on 20-inch centers.

During the process of application the overlying vegetative structure will be damaged (it will regrow!). The soil structure itself, to a depth of 12 inches, will be drastically altered. To prevent the loss of soil moisture and to reseal the soil (thus minimizing volatility and damage from wind), a soil compacter (cultipacker) will be required.

It is proposed that a drum emptying, cleaning, and disposal operation be established at the disposal site. Specifics on emptying the drum will depend upon how much efficiency is required in the operation. At the least, hoists and drums punches will be required.

A rinse system can be designed into the emptying operation. The rinse should probably be diesel fuel. No effort should be made to reclaim the drums. Instead they should be crushed and placed in a shallow burial. If the soil is strongly alkaline (pH 9 or 10), the metal will degrade via calvanic action.

CALCULATIONS AND COST ESTIMATES

ASSUMPTIONS: 2.3 million gallons of Orange

 8.6 pounds active ingredient/gallon

 2 gallons of rinse/drum of Orange (total 92,000 gallons diesel fuel)

 Rate will be 1,000 pounds active ingredient/acre (500 ppm).

 Application via one D-8 CAT or equivalent piece of heavy equipment.

 (Estimated cost of D-8 CAT plus operator is \$30.00/hour)

 Speed = 5 mph

 Eight shanks mounted on 20-inch centers, thus providing 13.33 foot swath.

CALCULATIONS: 1 mile swath = 1.61 acres

 gallons/acre = 123

 gallons/minute = 16.4

 gallons/hour = 986

 gallons/mile = 197

 5 miles of injecting = 1,000 gallons, approximately.

OTHER SPECIFICATIONS: Injection pump must be capable of pumping 25 psi (suggest obtaining a 50 psi pump).

 The pump must furnish 2.05 gallons per minute per shank (eight of them).

Therefore, for 2.3 million gallons of Orange, it will require 19,544 acres.

However, if retreating is acceptable (data indicate it is), then 9,772 acres will be required (less than 16 square miles).

TIME: 2,426 hours of application time will be required.

COSTS FOR D-8 CAT: The cost/acre for the D-8 CAT will be \$3.72.

The total for D-8 time (with operator) will be \$72,780.00.

OTHER EQUIPMENT COSTS: Drum Emptying Equipment = \$5,000.00

Drum Cleaning Equipment = \$10,000.00

Drum Crushing Equipment = \$5,000.00

2 X 1,000 gallon reservoir units
with flotation wheels = \$7,000.00

Soil compactor (cultipacker) = \$1,500.00

Eight-unit subsoil injector = \$1,500.00

Pump plus plumbing = \$1,750.00

Total \$31,750.00

MANPOWER REQUIREMENTS: Drum-emptying Operation = 2 men

(OTHER THAN D-8 OPERATOR) Drum-cleaning Operation = 2 men

Soil Incorporating = 3 men

General Utility = 1 man

Supervisor = 1 man

Total 9 men

If the operation requires 240 days (rough approximate), suggest salary be established on a basis of one year. Thus, labor estimate at \$15,000.00 per man is \$135,000.00. If a per diem of \$10.00/day/man, then total labor cost will be \$156,600.00.

TOTAL COST OF DISPOSAL OPERATION

D-8 CAT plus Operator = \$72,780.00

Other Equipment = 31,750.00

Manpower = 156,600.00

SUBTOTAL = \$261,113.00

Estimated Cost of Monitoring
for three years = 35,000.00
\$296,113.00

Estimated Total Outlay

OR \$300,000.00

SECTION VII: SITE CRITERIA AND IMPLICATIONS FOR SELECTION

During recent months it has become more apparent that the stigma attached to the disposal of Orange will make the task of finding a disposal site difficult, regardless of the technique employed. For this reason, it is important that the criteria for selection of a site for soil incorporation include not only physical and biological factors but also management and socio-political factors.

PHYSICAL FACTORS

From the standpoint of just physical considerations, the soil incorporation technique provides an array of alternatives as to the selection of site. In general, four major factors must be considered:

1. A minimum of 16 square miles must be available.
2. The site must be remote. It cannot be adjacent to lands currently in agronomic production. The actual amount of "buffer zone" will depend upon the type of crop and/or the use of the adjacent lands (e.g., recreation vs. irrigated alfalfa crops vs. dryland wheat. The alfalfa would be much more susceptible to either vapor or particulates blowing from the site).
3. The land must have a low-use potential, i.e., it should be marginal land. Moreover, the land should not be considered land that will be significantly productive in the foreseeable future.
4. Water resources must be sufficiently far away so as not to be contaminated. The actual distance will depend on annual rainfall

and soil type.

Once potential sites meet these criteria, the following should also be considered.

a. The topography of the land must be relatively flat with a uniform surface. The sub-surface injection will be applied by heavy machinery and at relatively high speeds (5 mph) and thus, rough, rocky terrain would be unacceptable. The net grade of the land should be less than one percent in order to minimize surface runoff. Acceptability of the grade will be related to soil porosity and vegetative density.

b. The texture of the soil should be sandy-loam or silty-sand. An acceptable soil porosity will be related to annual rainfall. High rainfall areas will dictate the need for less porous soils. The capacity for wind blow is influenced by texture. A light, sandy soil is more mobile than a soil having some clay binder.

c. The soil should have a pH of 8.5 to 9.5. This alkaline condition will minimize leaching of the herbicide.

d. The organic matter of the soil may be minimal. Obviously, a soil organic matter of 0.1 to 1.0 percent would be good; however, it is unlikely that these levels will be in areas that meet other requirements. From a political point of view, consideration may want to be given to enhancing soil degradation by the addition of other waste materials, e.g., sewage sludges or waste oils.

e. The area should not be characterized by rock outcrops or areas of marked deflation or dunes. The area should also have minimal surface erosion.

f. Data should be available on subsurface geology and hydrology. The distance below the surface to clay-pan or impervious rock should be known. If fault lines are present, the patterns of dips and strikes should be determined. Data on the water table for the whole site should be known. An area with a low rainfall (less than 12 inches) is acceptable. However, the distribution throughout the season of what precipitation may be important in considering depth of penetration of the herbicide. High precipitation over a short interval of time may move the herbicide down into the soil profile (very unlikely for it to move more than a few feet). A high annual evaporation rate will prevent accumulation of water on the surface, but at the same time this may enhance codistillation of the herbicides. Such "vaporization" will be minimized by the alkaline soil. Research by this author is currently in progress to determine the exact parameters required for codistillation of Orange.

g. Some additional items might include the availability of old "well logs" which might give soil profile data and the depth at which rock was found. The previous history of the site should be known so that if unexploded ordnance is present, the area can be avoided.

BIOLOGICAL FACTORS

The vegetation that characterizes a particular site is the result of many factors. Probably the most important factors would be precipitation and soil type. Land that has a low-use potential would typically have low annual precipitation and high soil pH. This "arid semi-desert" region would probably have temperature extremes in excess of 100°F in the

summer to freezing occasionally in the winter. Such a region would be vegetatively characterized by such shrubs as greasewood (Sarcobatus sp.), sagebrush (Artemisia sp.), winterfat (Eurotia sp.), rabbitbrush (Chrysothamnus sp.), saltbush (Atriplex sp.) and soapweed (Yucca sp.). Various species of cactus, small forbs, and native grasses will also be present. For use in the proposed program a shrub cover of 15-20% would be ideal.

It was emphasized in Section VI that both the heavy machinery and the herbicides are going to damage and/or kill the shrubs and forbs in the disposal area. However, this will take a few months and during this time native grasses will increase. Dr. Goulding has noted that grasses can be established right on the soil incorporated rows: since the herbicide has been placed beneath the surface, toxic effects to the grasses are minimal. The isolation of the site can be important in view of damage to the plants. Perhaps Dr. Boysie Day (11) has said it best:

I do not propose that the use of phenoxy herbicides is free of all hazards to non-target species. These materials are highly toxic to some plants, so much so that their use is prohibited or rigidly regulated in some agricultural areas. Minor drift and volatility of these herbicides can also affect sensitive vegetation outside of treated areas in range situations. However, such injury rarely goes unnoticed. If we see a paint-spattered automobile standing beside a freshly painted building, it requires no genius to discover what has happened. Similarly, the distinctive symptoms of injury to vegetation close to areas treated with 2,4-D and 2,4,5-T is just that obvious, and the cause of the damage is subject to the same preventive measures--learn how to do the job properly and be careful.

Moreover, it should be remembered that the dead shrubs will help stabilize the soil from wind blow.

Prior to initiation of the disposal program it will be important to have gathered vegetative data for a baseline study. The purpose of this is to give us a means of evaluating the change in the overall community following recovery of the site. Such baseline data as relative species density and vegetative cover will be required. Permanent linear transects should be established on and adjacent to the site. Aerial photography, including infrared pictures, should be made of the disposal area before, during, and after the disposal program. Permanent photo points should be established on the ground. Calculations on the "carrying capacity" of the site and an estimate of TDN (total digestive nutrients) should be made.

As the vegetation is affected by the herbicides, a profound influence will be exerted on the animal populations of the site. All available data indicate that toxicity of the agent will be of minor significance as compared to the destruction of the habitat. The toxicity of Orange was discussed in Section II. Research by Zielinski and Fishbein (51) indicate that of the formulations studied, the butyl esters of 2,4-D and 2,4,5-T disappeared more rapidly from body tissue of mice than did other ester formulations or the free acids. Moreover, the rapid elimination of the esters (2-24 hours) suggested that the herbicides were excreted unaltered from the animals. Surprisingly, Zielinski and Fishbein also noted that pretreatment of the animals enhanced the disappearance rate of the 2,4-D butyl ester. In view of the extreme toxicity of TCDD, concern will be voiced over the possible plant uptake, via the roots, of this material from the incorporated rows. Data by Isensee and Jones (21) have indicated

that TCDD uptake by oats and soybeans (a grass and a broadleaf) were very minimal, and the accumulation by plants was concluded to be highly unlikely.

As with the plants, baseline data will be required on animal species and populations prior to the initiation of the disposal program. Relative estimates should be taken of the rodent, mammal, and bird populations. The dominant species of insects and reptiles should be characterized. Tietjen (45), Keith, Hansen, and Ward (25), and Pimentel (37) have noted that treating vegetation with herbicides may alter the plant species composition, and thus the suitability of the habitat for certain mammals. However, Coulter (7) has suggested that herbicide treated areas may be used for "game food patches". This is a program in which crops (grains or native grasses) are planted in a treated area in the "wild" environment and are harvested by game or other wildlife. Coulter notes that maximum yield is not necessarily a consideration and that these "patches" can be established on undesirable sites. Krefting and Hansen (28) have noted that deer showed no preference for either untreated or herbicide-stimulated (2,4,5-T) branch growth on browse species.

Before leaving a discussion of biological factors, one additional idea should be proposed. If great concern is made over the effects on wildlife, it may be advantageous to employ a "striping" technique on the disposal site. This would involve leaving 1/4-mile strips of land untreated. Perhaps 10% of the area could be left untreated (thus, increasing the disposal area to approximately 18 square miles). This would allow many animal species to move to untreated areas, thus minimizing the damage to certain animal populations.

MANAGEMENT FACTORS

Management is the key to the success of this disposal program. The manager must be cognizant of such factors as:

1. The logistics of loading and unloading of the agent.
2. How to maximize injection of the agent, while minimizing the overall labor operations.
3. How to safely handle the agent and how to react to accidental spills.
4. What the requirements are for established roadbeds to and within the site.
5. What the requirements are for security of the disposal site.
6. What techniques can be used for site improvement. This would include the seeding of grasses and forages for wildlife and/or erosion control.
7. How to establish and effectively use a monitoring program for the site.

A monitoring program is essential; not only to provide data on the progress of soil degradation, but perhaps more importantly to provide assurance that contaminants from the disposal site are not causing an "ecological hazard" to the surrounding community. The monitoring program should include two major areas: (1) monitoring chemical and physical factors, e.g., levels of herbicides and extent of volatility or particulate movement; and (2) monitoring the effects of the disposal program on plants and animals.

The security requirement for the area will be influenced by the degree

of public access. The security may involve only an occasional surveillance. On the other hand, if there are anti-military factions in the adjacent communities, fencing may be required. The planting of dead animals on the disposal site by radical individuals would not enhance public assurance of the safety of the disposal program. Fencing may also be essential if the monitoring program detects residue levels of herbicides or contaminants in food chain components. This is extremely unlikely, but the manager of the site should be aware of it.

It is suggested that the management of the entire disposal program be submitted to a systems analysis. The use of a PERT flow system would help to identify points for decision and areas of commonality. This approach might eliminate duplication of efforts.

SOCIO-POLITICAL FACTORS

Throughout this entire proposal, reference has been made to the political environment requiring the disposal of agent Orange. Dr. Boysie Day (11) has perhaps summed it up by stating:

From the number and vehemence of published and spoken words in opposition to 2,4,5-T, the happiness occasioned by such a restriction (complete prohibition of use) should be widespread. . . I grant that it is of no political significance whether the alleged hazards of 2,4,5-T are real or imaginary. It is sufficient and justifiable to ban it when enough people want to ban it. The fact that this chemical has been extensively used in an unpopular war, combined with other doubts and suspicions, may yet turn the tide in its disfavor.

Some of the socio-political considerations that will influence the selection of a disposal site will include:

1. The distance of the disposal site from the point of origin of the agent. The selection of a dock, to which the agent must be brought, will need to be thoroughly studied.
2. The sensitivity of the areas through which the agent is to be transported.
3. The nature of the shipment itself. Certainly the transport of the nerve gas has taught the Department of Defense some lessons. The transport of the herbicide is critical. Everyday bulk shipments of herbicide cross the country. The transport of Orange would, by itself, be only a normal transport of herbicide. Whether the shipment is made in bulk or 300 drums at a time (railroad flatbed) will be an important decision. With proper site management, 4,000 gallons of Orange could be incorporated per day. Thus, shipment of 24,000 gallons (4,364 drums) could be transported on a weekly basis.
4. The place of storage of the agent prior to disposal will also be politically sensitive. If mass shipment is required, then storage at the disposal site will be most practical.
5. The final selection for the disposal site may well be in a state that has environmental laws reasonably compatible to the whole disposal program. This cannot be over emphasized: the nature and limitations of disposal laws incorporated into the state environment program must be thoroughly examined! They must be adhered to as closely as possible!

6. The amount and route of a public relations program. An excellent public relations effort will minimize the impact of the disposal program. Proper homework must be done prior to the releasing of any news report! Considerations in this area would include the involvement of state personnel in the monitoring programs and in key management positions.

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GLOSSARY

- ABSORPTION - Movement of a herbicide from the surface into a body (e.g., from the soil solution into a clay particle).
- ACID EQUIVALENT - The theoretical yield of parent acid from an active ingredient.
- ACTIVE INGREDIENT - Actual amount of toxic material in a formulation.
- AEROBES - Microorganisms that have an oxygen dependent form of respiration.
- CARRYING CAPACITY - The number of animals that a given area of land can support without damaging the vegetation.
- CODISTILLATION - Phenomenon resulting from simultaneous "vaporization" of the herbicide and rapid water evaporation.
- CONIFERS - Pine trees including spruce and fir.
- DRIFT - The movement of material outside the intended target area.
- ESTERS - Chemical compounds formed by the elimination of water between a molecule of an alcohol and a molecule of an acid.
- FACULTATIVE ANAEROBES - Microorganisms that can live either in the presence or in the absence of molecular oxygen.
- FORMULATION - A mixture of an active herbicide with carriers, diluents, or other materials.
- HERBICIDE - A chemical used for killing or inhibiting the growth of plants.
- LD₅₀ - The dosage required to kill 50% of the test organisms when given a single oral dose.
- PHYTOTOXIC - A term applied to any chemical that is toxic to plants.
- TERATOGENIC - A chemical causing the development of an abnormal fetus.
- VOLATILE - Refers to substances that evaporate or vaporize at ordinary temperatures on exposure with air.