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11901 Samuel Drive, Garden Grove, CA 92840-2546

Item ID Number	03721 ☐ **Not Scanned**
Author	
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Report/Article Title	Notes, Typescripts: Recommendations for Handling and Disposal of Military Herbicides [1970]
Journal/Book Title	
Year	0000
Month/Day	
Color	☐
Number of Images	64
Descripton Notes	Items were filed together under the label, "File 1. Recommendations for Handling and Disposal of Military Herbicides." Appear to be notes and other information used in Technical Notes AFATL-TN-70-3, July 1970, same title as above.

Total Rate on TEST AREA

ORANGE - 20,625.4 gallons
PURPLE - 16,164.2 "
WHITE - 3,908.1
264.0 PAU-7 1970
4,172.1

BLUE - 2,425.2 (1969 1 July - 20 Aug)
1,426.0 (PAU 7B MISSIONS
20 MAY - 28 MAY 70)
3,851.2

STULL - 1,716.0

EARLIER DATA (DATA PRIOR TO PAU 7B) WAS CALCULATED SO THAT AN ESTIMATE OF 204 gallons/A was delivered on a flight line.

White

A sewage disposal unit

→ circular, having the dimensions of 80-ft diameter and 6 feet deep

→ 30,171 cubic feet or ≈ 226,400 gallons.

or a concentration of active ingredient of white of 4000 ppm.

$$\frac{67\ ppm}{.5} = \frac{800}{x}$$

$$x = \frac{(.5)(800)}{67}$$

6 lbs/A/DAY

$67 \overline{)400}$
402

$6 \overline{)2,970}$ lbs = 495
24
57
54
30

495 days

MIN time for picloram would be 1 YEAR assuming that only photodegradation could occur. This would be utilizing a small unit.

Construction of a disposal site: ~~a~~
A pond having the dimensions of 6 acre feet.

Found that 440 mg in 8 hours –
660 mg in 12 hours

Picloram at 67 ppm = .5 lb/A/DAY
if 8000 ppm = 6 lbs/A/DAY
if 2 Acre-foot = 12 " "
min. of 247 DAYS.

Many commercially available sewage systems would have units with volumes of 1–2 Acre-feet.

1 cubic ft = 7.5 gallons $7.5\overline{)525{,}000}$ = 70,000 cubic feet

A 2-Acre-foot sewage disposal unit could be constructed (or if available) for photodecomposition of White. Data suggest that 120 drums of White could be effectively degraded in 250 days to humic acid and inert nitrogenous materials. This residue could then be utilized as fertilizer.

120 gal in 2 acre ft water
eff conc. 5000 ppm

$$\begin{array}{r} 70{,}000 \\ 6{,}600 \\ \hline 63{,}400 \end{array} \qquad \begin{array}{r} 650{,}000 \\ 6{,}600 \\ \hline 643{,}400 \end{array}$$

6. Chemical neutralizering techniques for ~~neutralization~~ disposal & spills. of herbicides are not available. However, this laboratory has investigated the use of activated charcoal for spillage of small quantities of herbicides. Our data indicated that 2000 pounds of activated charcoal (per acre ( ) could effectively bind (~~thus preventing movement~~) up to 8 gallons per acre of Orange or White. However, 5000 pounds charcoal/A were required to nullify the biological effects from contaminated soils ~~soils~~ at these rates. Data suggest that leaching from spills could be minimized by heavy applications of ~~activated~~ charcoal.

White

We do not recommend soil incorporation for white because of the persistence in the soil that would result.

We do not recommend incineration because to the best of our knowledge

1. No incinerator is available
2. 1000 C only 91.2 % was destroyed
3. cost
4. lack of data on biological degradation of picloram.

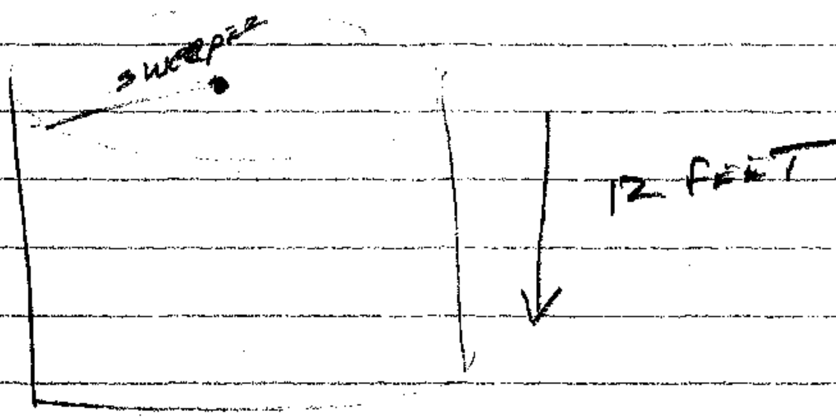
WHITE:

MIN

BARRONS → 0.5 lb picloram / A / DAY

1 gal of White contains .54 lbs

120 Drums x 55 = , 0 days

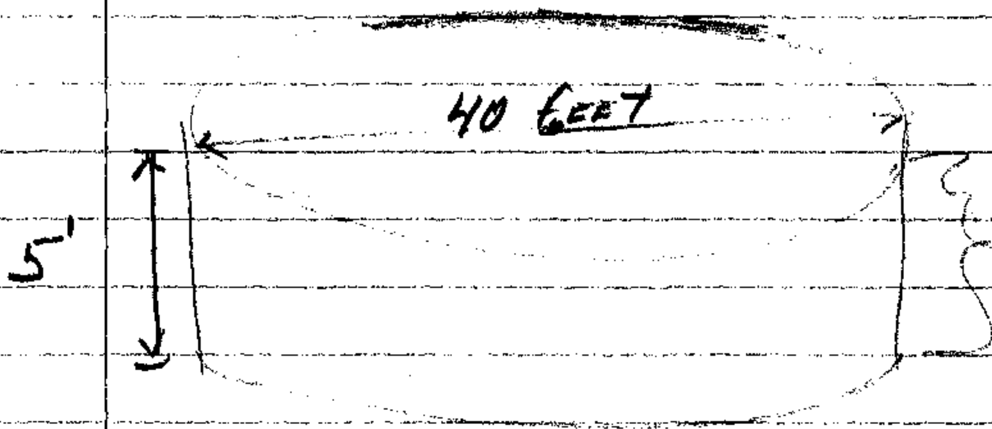


2,000 ppm = 525,000 gallons
use aeration via an agitator.

A coi

WE strongly recommended photo-decomposition. Under normal sunlight, get unidentified but non-toxic products. End product of 2,4-D would be humic acid & this is readily degraded by microorganisms.

Use of a commercially available sewage disposal system – should disposal systems would be "IdEAl" for such operations.



2,000 ppm
525,000 gallons
of water

V = 4

BARREL DISPOSAL (

Calculations

Active ingredient Data from
Henry Winders 27 July 70

Total

2,4-D	164,923	lbs	
2,4,5-T	148,496	lbs	
Picloram	2,252	lbs	— 4,171 gal White I calculate
Cacodylic Acid	11,934		
Malathion	305		

Aug - Sept 1970 — 400 gallons Blue

As of 1 Nov 1970 — 1,761 lbs Malathion

Calculations

If assume biodegradation of 1000ppm active herbicide than need to apply and incorporate 2,000 lbs of herbicide or
1000 ppm ai = 2,488 lbs Orange

or 232.5 gallons/acre

OR 148,800 gallons/square mile.

If need to dispose of 12,369 drums than would have 680,295 gallons, and hence, would require:

$$\frac{680,295}{148,800} = 4.572 \text{ square miles}$$

OR 2,926 acres

If applied in a zone 1/4 mile wide than would need a zone 18.3 miles wide.

One recommended procedure is to apply in 2-foot zones.

Therefore, 660 feet could be incorporate per width of 1/4 mile and hence would need a zone 36.6 miles long.

12,370
55
61,850
61,850
680,350

Quantity of Herbicide:

12,369 drums of ORANGE IN SEA
= 680,304 gallons
680,295

15,161 drums of ORANGE at Gulfport
= 833,855 gallons

120

6,500 gallons of WHITE IN SEA
= 118 drums

NO BLUE IN SEA.

680,304
8.6
408,1824
544 2432
5,850,614.4

1000 lbs/Acre = 2000 ppm ORANGE

250 lb/A = 500 ppm Orange

250
640
9000
1500
24,000 lbs Orange

2790.7 gallons
8.6) 24,0000
1721
680
602
780
774 600

57.4 drums/square mile
55) 2791
275
40
385
250

3,23,522 / 307,346 = 480 lb ai/A

325,419 / 95
640) 309,175 = 483 lb ai/A

1,002 ppm

966

6 increment = 167 ppm

4 ppm - 24 ppm

of the 501 lb ai/A

				PPM*
2,4-D & 2,4,5-T =	480	lb	=	960
picloram =	3	lb	=	6
Cacodylic Acid =	18	lb	=	36
	501			1,002.

* IN TOP 6-INCH OF SOIL

Thu. 1130 → Chamber of Com

1962 –
1968

2,4,5-T = 137,772 lb ai

2,4-D = 140,556 " "

picloram = 752 lb ai

Cacodylic acid = 1,055 " "

1969

2,4,5-T = 20,425
2,4-D = 24,241
picloram = 1,030
Cacodylic Acid = 6,464

1970 =

2,4-D = 528
Picloram = 143
Cacodylic Acid = 4,421
Malathion = 351 lbs.

Total 2,4-D = 165,325
2,4,5-T = 158,197
Picloram = 1,925 (2,252 ?)
Cacodylic Acid = 11,940 × 15.4 = 1,839 lb As

GALLONS

Total Orange = 20,626
Purple = 16,164
BLUE = 3,851
WHITE = 3,564
Malathion =

4-8 ppm - dioxin

20,626
16,164
36,790

11,940
154

Total Herbicide = 337,387

1 SQUARE MILE = 640 Acres
if 95% fell on that 640 Acres, then

527.2
x 95

95%

320,518 / 640 = 501 lb ai of herbicide / acre

if in top 6 inches = 250 ppm

WATER DISPOSAL

Rough Calculations

1 gallon of Orange = 8.6 lb ai/gallon

250 ppm in Solution = 1 gallon / 4,128 gallons of Solution

~~1~~ gallon of White = 2.54 lb ai/A

4 3560

$$\frac{1}{120} = \frac{2.54}{x}$$

$$x = (2.54)(120)$$

$$x = 305 \text{ gallons}$$

if ~~at~~ 250 ppm = 1220 gallons of water
if at 200 ppm = 1525
if at 100 ppm = 3,050 gallons
if at 1000 ppm = 305 gallons

To dispose of ~~100~~ 120 drums of White, then would have 5500 gallons of White & would require:

Required Concentration	Added to Gallons of Water	Required for Disposal
✓ 100 ppm	3,050	16,775,000 gallons
200 ppm	1,525	8,387,500 gallons
✓ ✓ 250 ppm	1,220	4,793,750
500 ppm	610	2,096,875
1000 ppm	305	1,048,438

2,000 ppm ← 524,219

If 1000 ppm active ingredient than need to apply and incorporate 2,000 lbs of herbicide

OR 1000 ppm = 2488 lbs Orange

OR 232.5 gallons / Acre

If applied at this rate per acre, than one square mile would receive 148,800 gallons.

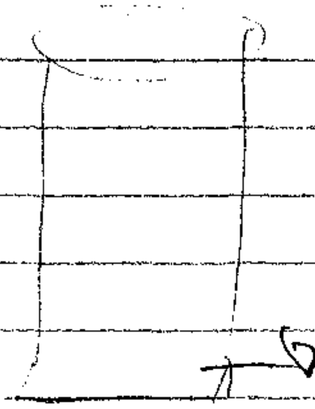
If in Vietnam 12,369 drums of Orange were available for disposal, than 680,295 gallons would [redacted] be equal to that quantity of drums.

$$\therefore \frac{680{,}295}{148{,}800} = 4.572 \text{ square miles}$$

4.572 square miles = 2,926 acres

If applied to a zone 1/4 mile wide, than would need to incorporate in a zone 18.3 miles long.

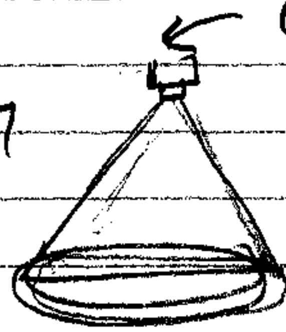
If appled in 2 foot strips



1/4 mile = 1,320 feet
if applied in 2 foot zones than could effectively treat 660 feet, and hence would need a distance of 36.6 miles.

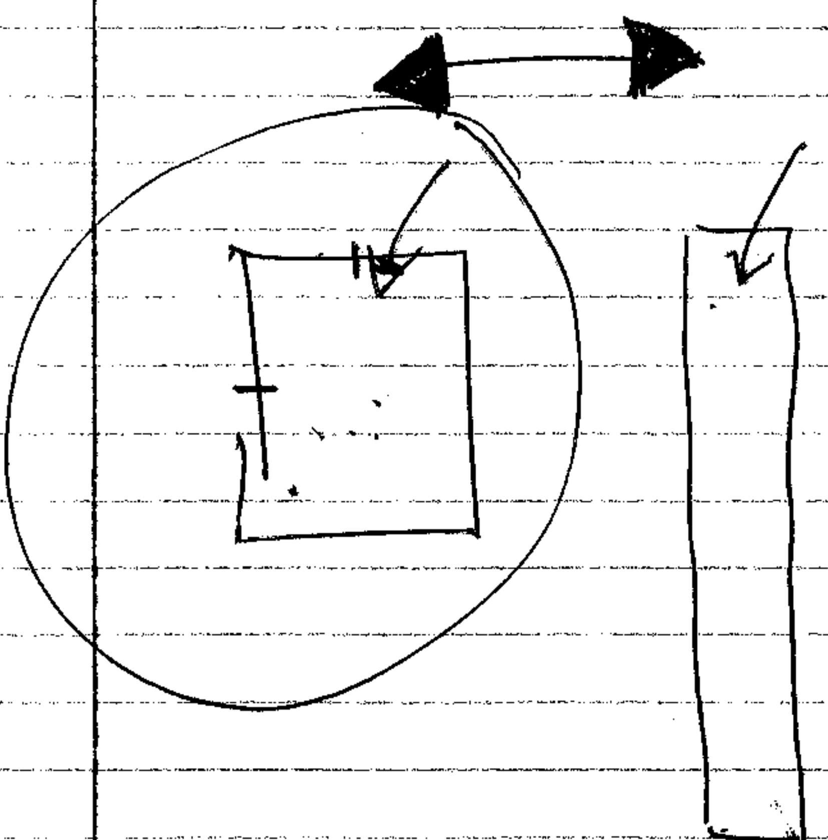
calibrated sprayer

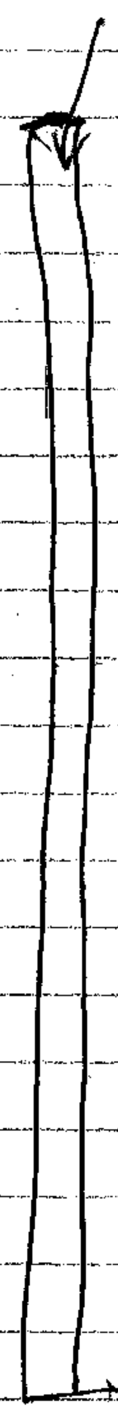
20'
→ 27



follow by a disk

(1) communication lines
(2) Base parameter
(3) Fire breaks
(4) along roads.
(5) Demilitarized ZONE





Eglin has received
37,700 gallons

SAFETY PROCEDURE - TO protect the pop- & MINIMIZE criticism

WATER MONITORING

~~The basis~~

Provided a certain recommendation this laboratory could furnish more specific details on any general comment.

The use recommendations and hence, handling are directed toward "commercial and or private use"

8557.0
1549
3268

1963 13,374 purple Total
95% = 12,705 OR 19.8 gal/A =

1964 = 8,788 gal Orange
95% = 8,348 gal OR 13 gal/A

Rough Calculations

To provide a concentration of 10ppm in 1 acre-foot of water 27 pounds of 2,4-D (acid equivalent) are required.

pg. 330 Toxicity: Pure 2,4-D acid at 100 ppm concentration caused slight mortality to fingerling bream and large mouth bass. The sodium salt was only slightly more toxic.
Fingerling bluegills suffered losses of 40 to 100% from the butyl esters of 2,4-D at concentrations of 1 to 5 ppm. Other work has also shown ester forms to be toxic to fish.

Length of row required for one acre

Row spacing	Length or Distance	
24 inch	7260 yards =	21,780 feet
30 inch	5808	17,424
36 inch	4840	14,520
42 inch	4149	12,445
48 inch	3630	10,890

Must consider the large quantities -

12,370 drums Orange
120 " White
"

Safest Solvent for flushing is isopropyl alcohol

Drums could be flushed & ~~[illegible]~~ flush disposed of. The drums could then be washed in soap & water & [illegible]ed.

Data on safety procedures for handling large quantities of concentrated herbicide are included in this report as well as recommended flushing agents and flushing techniques for herbicide containers.

RECOMMENDATIONS

FOR

BLUE

$$
\begin{array}{r}
3{,}851 \\
\times\ 10.9 \\
\hline
34659 \\
3851 \\
\hline
41{,}975.9
\end{array}
\qquad
\begin{array}{r}
5500 \\
\times\ 10.9 \\
\hline
49500 \\
5500 \\
\hline
59{,}950.0
\end{array}
\qquad
\begin{array}{r}
59{,}950 \\
\times\ .154 \\
\hline
239800 \\
249750 \\
59950 \\
\hline
8{,}732.300
\end{array}
$$

5,500 gal. = 59,950 lbs of Blue.
active ingredient
= 17,050 lbs of Organic Arsenic
= 8,732 lbs of Arsenic (15.4% of 59,950)

On grid delivered = 3,851 gal
41,976 lbs of Blue
3. 6,464 lbs of Arsenic
(15.4% of 41,976)

If 10 ppm Arsenic in soil this equal to 20 lb/A + to spread 8,732 lb of Arsenic at this Rate would Require 436 Acreas.
If 20 ppm As in soil this equal to 40 lb/A + to spread 8,732 lb As at this Rate would Require 218 Acreas.

$$
\begin{array}{r}
130 \\
\times\ .154 \\
\hline
520 \\
650 \\
130 \\
\hline
20.020
\end{array}
\qquad
\frac{15.4}{100}
\qquad
\frac{20}{4}
$$

1299
15.4) 200000
154
460
308
1520
1386
1340

On Eglin Spray Equipment testing grid we have disseminated 3,851 gal of Blue in the past 3 years, This represents 6,464 lbs of arsenic. Data from atomic absorption analysis confirmed that arsenic concentrations in the soil never exceeded 1.4 ppm. Leaching of Arsenic was detected to 5 ft in the soil. This leaching depth was expected because of the very low CEC of the soil.

IN Mississippi cotton field cacodylic acid is applied at rate of 22 lb/A. The maximum level selected as toxic to cotton is 100 lb/A (50 ppm).

We propose that the method of disposal of 5,500 gal (100 drums) of Blue would be soil incorporation. If a maximum allowable concentration of Arsenic in the soil was 10 ppm then the application rate would be 20 lb/A. If the maximum allowable concentration

If 208 acres had been
been treated

$$\begin{array}{r} 31.08 \\ 208\overline{)6,464} \\ \underline{624} \\ 224 \\ \underline{208} \\ 1600 \end{array}$$

31.1 lbs per acre
or 15.5 ppm

CEC < 1
only arsenic
2 ppm
1 ppm

As F

1 square mile =

In this country in Mississippi
MAX conc of Arsenic in
soil cannot exceed
100 lbs/A

specify a cation exchange capacity of 200%
safety margin

Select a soil containing a cation exchange
Capacity of at not less than 6 (milliequivalents
per 100 grams of soil). This would
give a 200% safety margin
in terms of soil adsorption.
Soils in SEA are characterized
by high kaolinite clay content,
CEC of this magnitude should

available, however the addition of activated charcoal would enhance this CEC; likewise the addition of

allowable

6 Incineration of Blue is <u>not recommended</u>. ~~since~~ Since Blue contains organic forms of arsenic, the end result of ~~a~~ incineration would be the accumulation of an arsenic residue (inorganic arsenic) that would be 40 to 100 times more toxic than the original herbicide.

Spray equipment are already available in SEA for such ~~an~~ operation. The most important factor is the selection of a suitable site. The area should ~~have~~ be a minimum of 218 Acres. The area should not have direct drainage sites. The soil should have a CEC of not less than 6 (most soils in tropical areas have a CEC of 9.4). The CEC can be determined by any agricultural institution.

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7. Biological Degradation

It has been established for several years that the rate at which herbicides disappear from the soil is largely dependent upon their resistance to metalbolism by soil microorganisms.

Environmental factors that influence microbial degradation of herbicides are temperature, pH, moisture content, oxygen content and organic matter or fertility (10,33,37,47). Generally the microbial population of a soil has its greatest capacity for degradation of herbicides under the following conditions: (a) a soil surface air temperature between 75 and 95 F; (b) a soil pH between 5.5 and 7.5; (c) a moisture content that is 50 to 70% of the water holding capacity of the soil; (d) a well aerated soil that results from the plowing or loosening of the top 6 to 12 inches of soil; and (e) an organic matter content that yields a carbon to nitrogen ratio of about 10:1 resulting from the incorporation of plant residues or organic fertilizers into the soil. Also, the addition of well balanced mineral fertilizers tends to enhance soil fertility and increase microbial activity.

a. Phenoxy herbicides

There is considerable evidence available to show that 2,4-D contained in Orange (and White), is rapidly decomposed in most soils. The metabolism of this herbicide in soil has been investigated more than any herbicide. Many bacteria have been isolated that are capable of using 2,4-D as a primary energy source (1,33). If 2,4-D were applied to a moist loam soil under summertime temperature (75 to 95 F) at a rate of 0.5 to 3 lb/A it would disappear in 7 to 30 days (33). If applied at rates of 4 to 55 lb/A it would probably disappear in one to three months (17,29,41). If 2,4-D were applied to the soil at a concentration of 500 ppm (1,000 lb/A) and disappeared at a rate proportional to the breakdown of 55 lb/A, the time required for inactivation is calculated to be 5.6 years. There is no definitive field data available concerning the time required to detoxify concentrations of 500 ppm or greater. However, some evidence indicates a more realistic time for inactivation of 500 ppm would be one to two years.

Soil microorganisms have remarkable adaptive powers and several people have shown that microorganisms can, by adaptation or mutation, alter their metabolic pathways for a more efficient utilization of herbicides (8). Colmer (14) found that the tolerance of bacteria to 2,4-D could be increased by serially subculturing in increasing concentrations of the herbicide. Newman <u>et al.</u> (36) and Rogoff and Reid (38) discovered that 2,4-D disappeared from soil more rapidly with the second application. Walker and Newman (49) found in laboratory tests that 100 ppm 2,4-D was decomposed in three to five days. They noted subsequent treatment of the same soil with 1,000 ppm resulted in decomposition occurring in 10 to 14 days. When microorganisms are exposed to a relatively high concentration of a foreign material there is usually a lag period before utilization of the materials begins. This lag period represents the time required for the microorganisms to become adapted. In a soil freshly treated with 100 ppm of 2,4-D, 20 days were ~~may be~~ required for 80% detoxification whereas in the same soil previously treated with 2,4-D ~~will bring about~~ 80% detoxification occurred in three days (1).

Persistence of 2,4,5-T in soils is two to three times longer than 2,4-D (17,33). The addition of another chlorine atom to the 2,4-D molecule results in a compound that is not readily metabolized by soil microorganisms. The metabolism of 2,4,5-T by soil organisms has not been investigated as much as 2,4-D metabolism. While several bacteria have been isolated that degrade 2,4-D, very few organisms have been identified as having the ability to breakdown the 2,4,5-T molecule (1).

Some soil microorganisms are quite susceptible to phenoxy herbicide concentrations greater than 50 ppm (8,21). Smith et al. (43) found nitrate and nitrite-forming organisms inhibited by 100 ppm of 2,4-D, but recovery occurred in 10 to 40 days. At a concentration of 500 ppm recovery of nitrite organisms did not occur 90 days after treatment. Arnold et al. (4) found *Aspergillus niger* to be inhibited by 50 ppm of 2,4-D, however, the fungus seemed able to degrade the herbicide. The amounts of phenoxy herbicides required to inhibit many microorganisms is very high. Arvik et al. (5) found that 2,4-D did not seem to inhibit three soil algae at a concentration less than 400 ppm. Walker and Newman (49) worked with a soil bacterium requiring 5,000 ppm 2,4-D for growth restriction. Johnson and Colmer (30) observed that growth of *Bacillus cereus* was inhibited by 500 ppm of 2,4-D but concentrations of less than 5,000 ppm had little effect on *Pseudomonas fluorescens*. They found concentration of 20,000 ppm of 2,4-D was required to completely inhibit gelatin ammonification is a soil suspension. Rogoff and Reid (39) isolated a *Corynebacterium* sp. having the ability to decompose 1,000 ppm of 2,4-D in 3 to 5 days. Shennan and Fletcher (42) 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 of 2,4-D. Twenty-four organisms required 10,000 ppm of 2,4,5-T for growth restriction.

Other information useful in determining what might happen to the microbial population when in contact with high herbicide concentrations is work of Breaseale and Camper (11). They analyzed the bacterial, fungal and actinomycete population of a soil that had received 20 lb/A/year of 2,4-D for four years. The fungal and actinomycete populations were not affected; however, the bacteria showed a 50% reduction. Koike and Gainey (34) found that agronomic concentrations of a mixture of activated diesel emulsion and 2,4-D did not inhibit nitrifying bacteria. Higher concentrations (50 lb of 2,4-D and 5,000 gallons of the diesel emulsion) inhibited nitrification for 8 to 16 weeks. The total number of bacteria increased.

b. By-Products of 2,4-D and 2,4,5-T biological degradation

From time to time concern is expressed as to what might be the effects on water supplies of the products of 2,4-D and 2,4,5-T microbial decomposition. The reason is that phenols have been discussed as a possible by-product of decomposition. Winston (60) studied the degradation products of 2,4-D and 2,4,5-T and concluded that decomposition under natural conditions does not result in the formation of the corresponding phenols. Phenoxy herbicides were found to decompose into carbon dioxide, inorganic chloride ions and water.

c. Picloram

It is relatively well known that picloram is one of the most persistent herbicides. Goring et al. (23) sampled soils from California, South Dakota, Kansas and Minnesota that had received from 1.4 to 4.2 lb/A of picloram. Picloram losses ranged from 58 to 96 % within one year after application. Estimated half-lives for picloram ranged from 1 to 13 months. The highest concentrations were usually found in the top 12 inches of soil. At normal field application rates, picloram may penetrate two to four feet in the soil with deepest penetration occurring in light soils that are low in organic matter (23,27,28). Grower (45) found the half-life for 1 ppm of picloram to be about six months in a heavy clay topsoil.

Soil microorganisms seem to exhibit little ability to rapidly degrade picloram. Many microorganisms are capable of a slight degradation (1.2 to 0.2% of 1 ppm in 63 days) but no organism has been found that can use picloram as a good energy source (53). Picloram is relatively nontoxic to a wide variety of soil microorganisms, but a few, such as soil algae, may be affected by low (50 ppm) concentrations (5).

Goring et al. (24) found in several tests that picloram at 1,000 ppm did not inhibit 28 soil fungi, 10 bacteria and 2 actinomycetes. They also found that 1,000 ppm did not appear to have a significant effect on the soil microbial population. Nitrogen transformation experiments showed that 1,000 ppm of picloram gave a 50% inhibition in the conversion of ammonium to nitrate, but the conversion of nitrite to nitrate was not affected. Tu and Bollen (46) have also studied the effects of ~~picloam~~ picloram on soil fertility processes. Their results tend to compliment those of Goring et al. (24), ~~and~~ in addition they found some stimulating influences when 1 to 10 ppm was applied to the soil.

d. Organic arsenicals

There is very little information available on the interrelations between organic arsenicals and microorganisms in the soil. ~~Diskens~~ Dickens and Hiltbold (18) monitored the breakdown of disodium methanearsonate (DSMA) in different soils. They concluded that methanearsonates are decomposed under aerobic soil donditions and that the amount of organic matter available for microbial activity has a direct effect on the rate of decomposition. Von Endt et al. (48), working with monosodium methanearsonate (MSMA), also discovered that the amount of organic matter greatly influences degradation of an organic arsenical. In three weeks decomposition of MSMA was 10% in a soil with 3.9% organic matter and 1.7% in a soil with 1.6% organic matter. Arsenate was detected as one of the products of MSMA breakdown.

There is considerable evidence to indicate that cacodylic acid or sodium cacodylate may be partially converted to arsenic gases (arsine or trimethylarsine) in the soil (2). These gases have a garlic like odor and have often been detected when soil fungi are grown in the presence of arsenic compounds (12, 44). However, the precise potential of cacodylic acid conversion and the subsequent loss of arsenic from the soil by gas production is not clear at the present time.

Many microorganisms can withstand high concentrations of organic arsenicals. Zabel and O'Neil (54) found that 2,000 ppm of either cacodylic acid or sodium cacodylate resulted in minimal inhibition of two bacteria and two fungi. Hunter (unpublished data) noted a 50 to 70 % reduction in growth of five soil fungi when incubated in the presence of 200 ppm arsenic supplied as 1,570 ppm of the military herbicide Blue.

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AFATL-TN-70-3

RECOMMENDATIONS FOR HANDLING AND DISPOSAL OF MILITARY HERBICIDES

ASSESSMENTS BRANCH
NON-EXPLOSIVE MUNITIONS DIVISION

TECHNICAL NOTES AFATL-TN-70-3

JULY 1970

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Air Force Armament Laboratory (ADLMA), Eglin AFB, Florida 32542.

AIR FORCE ARMAMENT LABORATORY

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EGLIN AIR FORCE BASE, FLORIDA

RECOMMENDATIONS FOR HANDLING AND DISPOSAL OF MILITARY HERBICIDES

Alvin L. Young, Captain, USAF
John H. Hunter, Captain, USAF

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Air Force Armament Laboratory (ADLMA), Eglin AFB, Florida 32542.

TABLE 1. A description of the herbicides applied to Test Area C-52A including military code, trade name, common name and formulation.

Military Code	Trade Name	Common Name	Formulation
Orange or Purple	Brush Killer	2,4-D, 2,4,5-T	Mixtures of the n-butyl and/or isobutyl esters of 2,4-D (2,4-dichlorophenoxyacetic acid) and 2,4,5-T (2,4,5-trichlorophenoxyacetic acid)
Pink	2,4,5-T	2,4,5-T	60% n-butyl ester and 40% isobutyl ester of 2,4,5-T
White	Tordon 101	2,4-D, picloram	10.2% of the triisopropanolamine salt of picloram (4-amino-3,5,6-trichloropicolinic acid), 39.6% of the triisopropanolamine salt of 2,4-D, and 50.2% inert ingredients (primarily triisopropanolamine).

Comments

The literature may support certain techniques for disposal, but it should be recognized that optimum conditions for disposla almost never occur, thus even the best xxxxxx recommmendations cannot account for all the variables required for either minimum effects on the environment nor the complete degradation of the agent.

for Orange
Military formulation is different from the commerical formulation for brush killer. The difference is in the esters. Likewise, Orange is more concentrated. The difference in formualtion is what limits its usd in forest programs. Of course, the current restrictrion on Oxxx 2,4,5-T prevents dilution of the formulation for use around homes and/or water supply areas.

We must be concerned with the ultimate fate of these materials in relation to their residual nateure in soil, potential for run-off in water , and their subsequent effect on the ~~food chain~~ ecological and/or environment [illegible] disposal.

The residual activity of the herbicide must eventaually be a function of the concentration related to the technque employed for disposal. This report, then, will attempt to show potential mechansims of disposal, and how certain modifications can be incorporated to enhance teh degredation (or technique).

Each technique will be described with consideration ~~of~~ for agent & conditions for their disposal.

Hawks ( ) has shown that 2,4-D was much more resistant to leaching from alkali soil than from a peat soil.

Hernandez and Warren ( ) found that ~~2,4-D was~~ high organic matter content in the soil reduced the movement of 2,4-D by leaching.

Newman, Thomas, and Walker ( ) found that the decomposition of 2,4-D and 2,4,5-T in soil was charactorized by a lag period of no decomposition followed by complete decomposition. The lag period increased from 14 days at the 0- to 6-inch depth to 42 days at the 18- to 21-inch depth. The lag period was shorter and decomposition more rapid for a second application.

over

2,4-D persisted less than 6 weeks while 2,4,5-T persisted more than 19 weeks.

~~Romeiro, L. and H. A~~

Rogoff and Reid ( ) noted that as much as 1000 ppm 2,4-D could be decomposed in 3 days in cultures of a Coxyne bacterium species, and 80% of the 1,000 ppm could be decomposed in 4 hours by resting cells that were suspended in a solution in phosphate buffer at pH 7.1. Chloride ion is formed quantitatively from the compound.

Day, Johnson and Dewlen ( ) found that three relatively low volatile 2,4-D esters and 2,4,5-TP low volatile ester were sufficiently volatile under comparatively high-temperature daytime conditions to cause severe injury to large crop areas surrounding sprayed plots.

ROUTING AND TRANSMITTAL SLIP		ACTION
1 TO (Name, office symbol or location) Mr. Vandeventer	INITIALS	CIRCULATE
	DATE	COORDINATION
2	INITIALS	FILE
	DATE	INFORMATION
3	INITIALS	NOTE AND RETURN
	DATE	PER CON-VERSATION
4	INITIALS	SEE ME
	DATE	SIGNATURE

REMARKS

Attached is a brief discussion of soil incorporation and biological and chemical breakdown of 2,4-D and 2,4,5-T. This information is furnished as background material for disposal of herbicides. This information was assembled by Capt. J. H. Hunter, Ph.D. plant pathologist and Capt. A. L. Young, Ph.D. herbicide physiologist (present address DFLS, USAF Academy, Colo. We feel that soil incorporation is a workable method for disposal and will be glad to furnish more detailed information.

Do NOT use this form as a RECORD of approvals, concurrences, disapprovals, clearances, and similar actions.

FROM (Name, office symbol or location)	DATE
Capt. Hunter	4 Jan
	PHONE 872-2909

OPTIONAL FORM 41
AUGUST 1967
GSA FPMR (41 CFR) 100-11.206

GPO : 1968 O—314-638 5041-101

Vandeventer later (1 April) sent write-up to Hq. USAF.

DISCUSSION OF SOIL INCORPORATION AS A
MEANS OF HERBICIDE DISPOSAL

Incineration seems to be an ideal method for disposing of Orange stockpiles; however, disposal by soil incorporation should be considered for the following reasons: 1. Soil incorporation has definite cost advantages. 2. Soil incorporation offers an alternative disposal method for those areas where incinerators are not available.

There is a great deal of information available on biological breakdown of 2,4-D and 2,4,5-T in laboratory experiments. Much of this information is very useful for predicting what might happen when relatively high concentrations of 2,4-D or 2,4,5-T are applied to a soil incorporation site. Conversely a certain amount of caution must always be used when extrapolating laboratory data to the 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 2,4-D and other compounds. A portion of Dr. Gouldings annual progress report is enclosed.

Data obtained on soil persistence of large quantities of 2,4-D and 2,4,5-T is also available from the Eglin AFB one square mile spray equipment test grid that was used from 1962 to September 1970. This area was sprayed with approximately 21,265 gallons of Orange and 16,164 gallons of Purple during a seven year period (1962-1969). The area also received

4,172 gallons of White between 1967-1970. In May 1970, plant bioassays indicated that the maximum concentration of Orange or Purple 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 1,500 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. A concentration of Dioxin of less than 0.0005 ppm was detected in the soil in December 1970.

One of the major advantages of soil incorporation techniques is the many alternatives available as to the selection of the site. Areas along communication lines, base perimeters, fire breaks, roadsides are all potential disposal sites. The site should be level to avoid direct run-off. The soil should be characterized by having a pH greater than 6.5 (either naturally or amended with lime) and an organic matter content of at least 1%. Ideally the site should be plowed and fertilized before herbicide application and then fertilized periodically after herbicide incorporation. The area should be seeded with native grasses as soon as herbicide levels are low enough to allow for growth of the grass. Orange (preferably that with a dioxin content of less than 5 ppm) could be incorporated either into alternate two-foot strips or sprayed evenly over an area at a concentration of 500 to 1,000 ppm (2,000 lbs or 232 gallons per acre). If, for example, a power line right-of-way with a width of 100 feet was used, approximately 4 drums/150 yards or 48 drums/mile could be incorporated. The incorporation could be done by use of calibrated spray rigs mounted on military heavy equipment. In certain areas evaporation of ester formulations of 2,4-D or 2,4,5-T might be a problem but in these areas the herbicide could be injected below the soil surface or plastic covers could be applied.

BIOLOGICAL DECOMPOSITION OF 2,4-D AND 2,4,5-T IN SOIL

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.

There is considerable evidence available to show that 2,4-D as contained in Orange is rapidly decomposed in soils. The metabolism of this herbicide in soil has been investigated more than any herbicide. Several bacteria have been isolated that are capable of using 2,4-D as a primary energy source (1,2).

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 (2). If applied at rates of 4 to 55 lb/A, it would probably disappear in one to three months (3). If 2,4-D were applied to the soil at a concentration 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.

Persistence of 2,4,5-T in soils is usually two to three times longer than 2,4-D (3), and very few organisms have been identified as having the ability to break down the 2,4,5-T molecule (1).

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 (4). 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 (1) 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 (5) 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. (6) and Rogoff and Reed (7) discovered that 2,4-D disappeared from soil more rapidly with the second application. Walker and Newman (8) 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. (9) added a mixture of 2,4-D and 2,4,5-T (similar to 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 CO_2 in 56 days. It also appears that mixtures of 2,4-D and 2,4,5-T are more rapidly degraded than are the single compounds.

R. L. Goulding is presently conducting field research with soil disposal of waste 2,4-D at rates as high as 1,000 lb/A. Dr. Goulding has seen a marked reduction of 2,4-D in his plots during a one year period (personal communication).

There are some microorganisms that are susceptible to phenoxy herbicides (2,4-D and 2,4,5-T) at concentrations of about 50 ppm (4). However,

R. L. Goulding is presen

most microorganisms are resistant to high concentrations. Shennan and Fletcher (10) 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. (9) 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.

2. By-products of 2,4-D and 2,4,5-T biological degradation.

From time to time, concern is expressed as to what might be the effects on water supplies of the products of 2,4-D and 2,4,5-T microbial decomposition. The reason is that phenols have been discussed as a possible by-product of decomposition. Winston (11) studied the degradation products of 2,4-D and 2,4,5-T and concluded that decomposition under natural conditions does not result in the formation of the corresponding phenols. Phenoxy herbicides were found to decompose into CO_2, inorganic chloride ions and water.

3. Chemical disposal of herbicides.

From a field operations point of view, it would be desirable to have available a chemical neutralization technique which could handle normal disposal and accidental spills. Data on chemical neutralization techniques is limited.

Witt et al. (12), in their discussion on a waste pesticide management system, noted that residue of herbicides in used containers could, with time, be degraded by alkaline, acid, or metal catalyst treatment. However, they neither presented a time table for destruction nor data to substantiate their statement. Kennedy, Stojanovic, and Shuman (13), subjected the herbicides 2,4-D and picloram to selected concentrations of five different chemicals with the objective either to partially degrade or to decompose the herbicides. Solutions of the herbicides were treated with three different concentrations of hydrogen peroxide, nitric acid, sulfuric acid, sodium hydroxide, or ammonium hydroxide. Their results indicated that only sodium hydroxide had an effect on the herbicides. The herbicide 2,4-D was hydrolyzed to the sodium salt, while picloram was decarboxylated and the chlorine present was replaced by a hydroxyl group. The bioactivity of these products was not evaluated, but presumably, in the case of 2,4-D, the herbicidal activity was not altered. They concluded that acid or alkaline hydrolysis was not complete in any case for the lengths of time studied (24 to 36 hours). N. A. Hamme (USAF Armament Laboratory, Eglin AFB, Florida, unpublished data) determined if the herbicidal effects of Orange could be chemically destroyed by oxidation and/or hydrolysis. Eight chemicals (benzyltrimethyl ammonium methoxide, calcium hypochlorite, lithium hydroxide, potassium permanganate, sodium hydroxide, ammonium hydroxide, sodium bisulfite, and tetramethylammonium hydroxide) were added to separate solutions of Orange, mixed thoroughly on a mechanical shaker, allowed to set a minimum of 24 hours, and then bioassayed for herbicidal activity by spraying tomato plants. His results showed, as determined by bioassay techniques, that no apparent degradation of Orange occurred in the presence of any of the chemicals tested.

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EFFECT AND PERSISTENCE OF HERBICIDES APPLIED TO SOIL IN PUERTO RICAN FORESTS

C. C. Dowler, W. Forestier, and F. H. Tschirley
~~XXXXX~~ WEED SCIENCE 16:45-50. 1968
United States Department of Agriculture

Inseparable from the biological effect of herbicides applied to the soil are their movement and persistence. Factors such as rainfall, physical and chemical characteristics of the soil, microorgandsms, chemical characteristics of the herbicides, and method of application may influence herbicidal movement and persistence.

The soil type at the Guanica Commonwealth Forest is Jacana clay. It is an alluvial soil normally less than 36 inches deep, with very low permeability. The vegetation is xerophytic. The annual rainfall is approximately 30 inches, which occurs largely from July to October.

The soil type at the Maricao Commonwealth Forest site is Nipe clay, a permeable, well-drained, lateritic soil derived from serpentine. The vegetation on this site is moist tropical forest. Mean annual rainfall is estimated to be about 90 inbhes and is distributed throughout the year.

The soil type at the Luquillo Nation Forest site is Low Guineos clay loam, a plastic clay with poor internal drainage. The vegetation is a tropical rain forest with a mean annual rainfall of over 100 inches. The highest rainfall normally occurs from July to October, but droughts are unknown.

Soils, as described above, were treated with 3, 9, and 27 lb/A picloram. The downward movement of the herbicide and its persistence in the soil were studied by sampling 3,6, and 12 months after treatment. Samples were taken in depth increments of 6 inches to a total depth of 48 inches.. The soil samples were bioassayed using cucumber.

Results indicated that after ~~xxx~~ two years residues of picloram were detectable. The persistnce of the herbicide was greatest in the driest area (Guanica) and least in the wettest area (Luquillo). One year after application, the residue of picloram in plots treated at 27 lb/A remained in relatively high concentrations at all test sites, as determined by the cucumber bioassay test. The presence of picloram in plots treated at 9 lb/A could be easily detected 1 year after treatment, but the concentrations were about 10 times less than in plobs treated with 27 lb/A. The residue data for all locations indicated a trend for all the herbidide to dissipate more rapidly in the top 12 inches of soil.

There did not appear to be any relation between herbicidal residue and invading species. For example, several species such as <u>Psychotria berteriana</u> were extremely susceptible to initial application of herbicides, but they were found on all treated plots 18 months after application.

PICLORAM RESIDUES 12 MONTHS

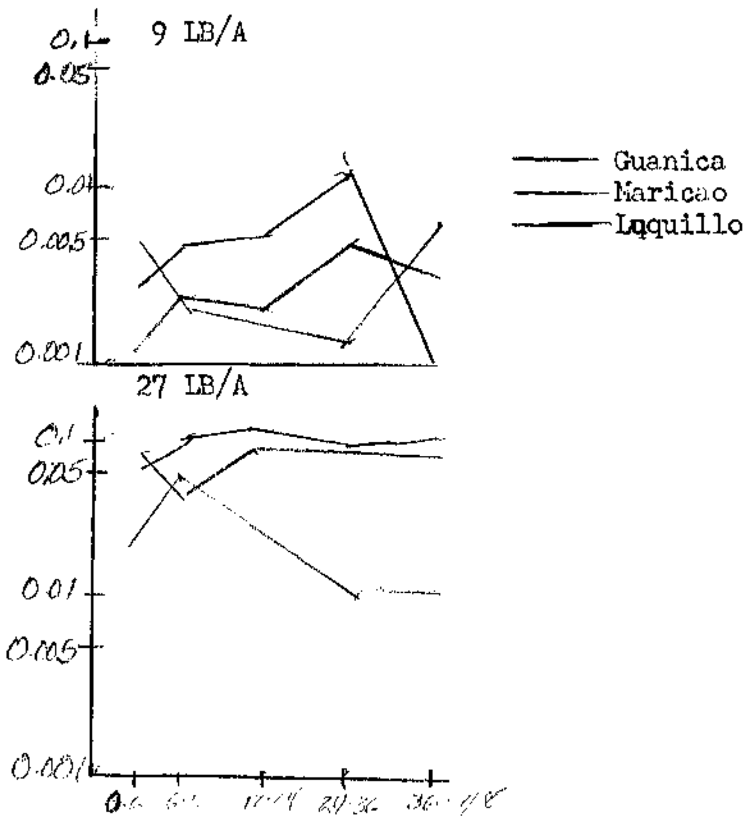


FIGURE 4. Picloram residue at various depths in three forest areas of Puerto Rico 12 months after application.

LOSS OF 2,4-D IN WASHOFF FROM CULTIVATED FALLOW LAND

A.P. Barnett, E. W. Hauser, A. W. White, and J. H. Holladay
WEEDS 15:133-137. 1967
USDA,ARS

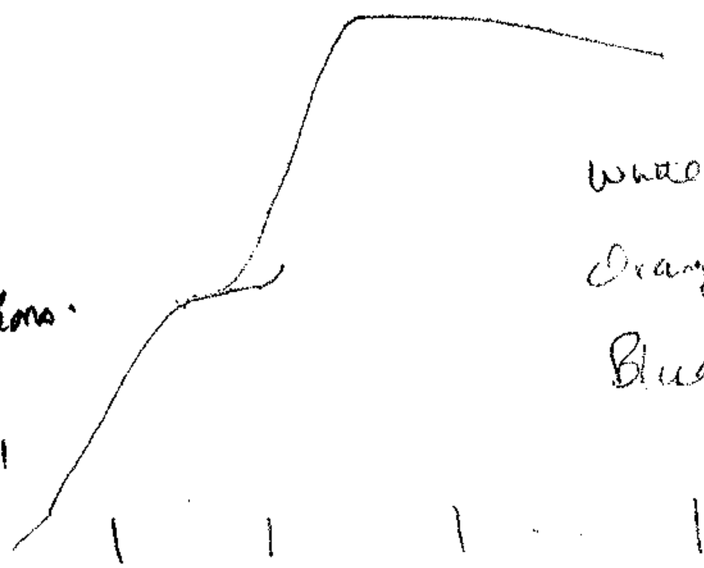
Quantitative information concerning the movement of herbicides in washoff from agricultural lands is needed. (The term "washoff" is used to describe the water-soil mixture as it erodes from the land and to distinquish it from its separate parts, i.e., runoff and eroded soil.

Quantitative measurements were made by cucumber root bioassay of 2,4-D contained in washoff from cultivated fallow Cecil sandy loam soil. Formulations of 2,4-D included iso-octyl and propylene glycol buty ether esters and an alkanolamine salt of the ethanol and isopropanol series. The 2,4-D applied at rates of 2.2 and 4.4 lb/A was assayed in washoff and as residue in the soil. The concentrations of 2,4-D in washoff were positively correlated with the rate applied, were greates early in each storm, and decreased with duration of the storm. The iso-octyl and butyl ether ester formulations of 2,4-D were far more susceptible to removal in washoff than the amine salt. When the amine salt was used, 2,4-D concentrations were less than 1 ppm in the washoff, even in the early stages of runoff, whereas concentrations of 4.2 ppm were measured using an iso-octyl ester formulation of 2,4-D. When a direct comparison was made between the butyl ether ester and amine salt forms of 2,4-D, ester or amine losses were respectively, 13 and 4% following a 1-year frequency storm and 26 and 5% following a 100-year frequency storm. Soil bioassays showed that most of the 2,4-D remained in the surface 3 inches of soil.

The differences observed in the susceptibility of the amine and ester sources of 2,4-D to loss by washoff probably are related to the physical properties of the applied solutions. Aldrich and Willard (Aldrich, R. J. and C. J. Willard. 1952. Factors affecting the preemergence use of 2,4-D in corn. WEEDS 1:338-345) pointed out that the amine forms a true solution with water, wheras the ester is relatively insoluble and forms an emulsion. They observed that the amine form leached more readily from soil surfaces than did the ester. This would suggest that the ester form, by being retained at the soil surface, would be more subject to losses in washoff.

Research currently in progress by this laboratory (Harrison and Young) has indicated that activated charcoal is effective in reducing the biological activity of Orange in sandy soils. Concentrations up to 8 gal/acre were completely inactivated by 8000 lb charcoal/acre in bioassay experiments. According to these data, charcoal could possibly be used as a means of holding Orange in the soil without causing biological damage while it is being degraded by microorganisms. It might also be used as a barrier beneath the soil to prevent herbicides from leaching into water supplies.

Federal



White - 8 gal 3,000

Orange " 4,000 lbs

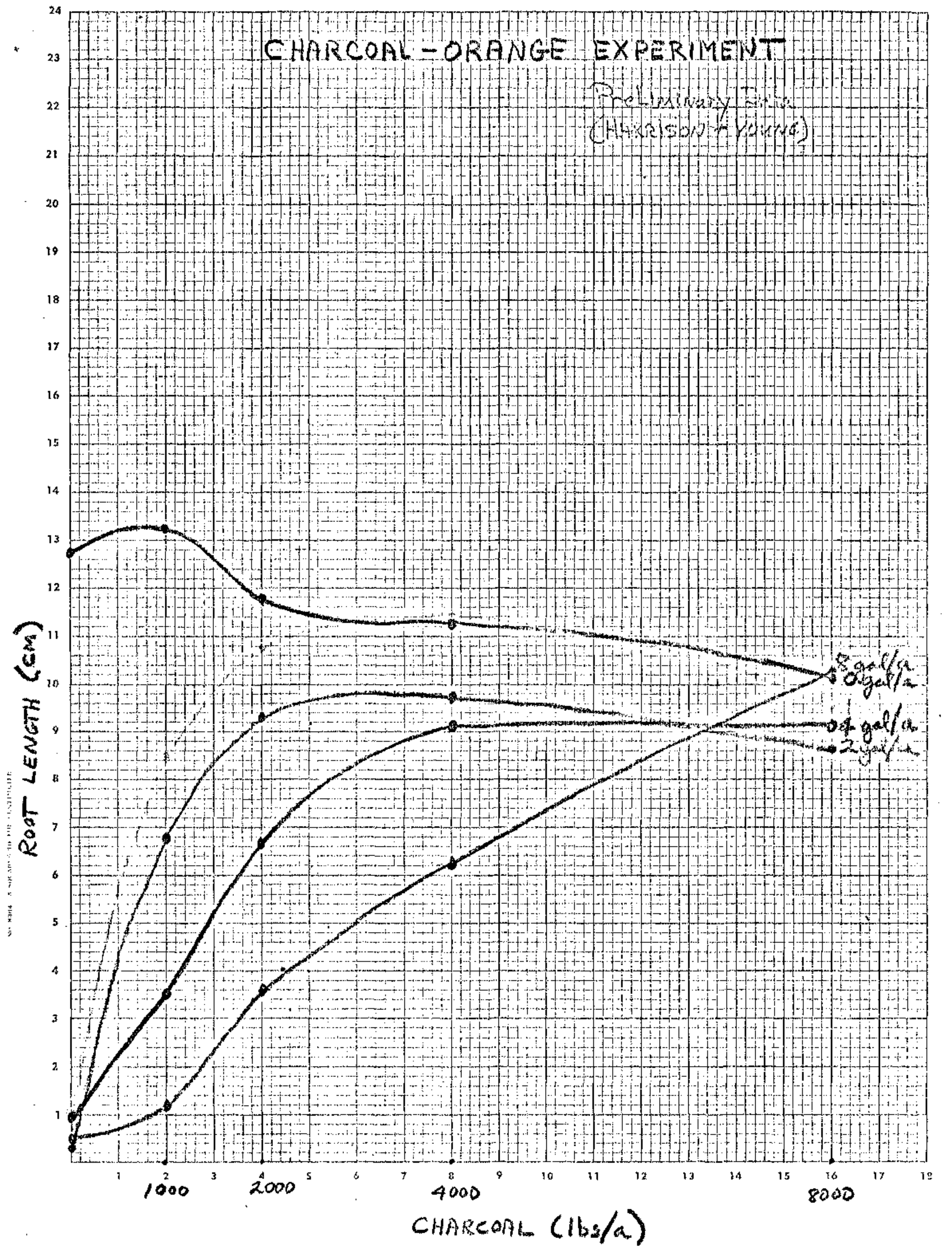
Blue - no effect

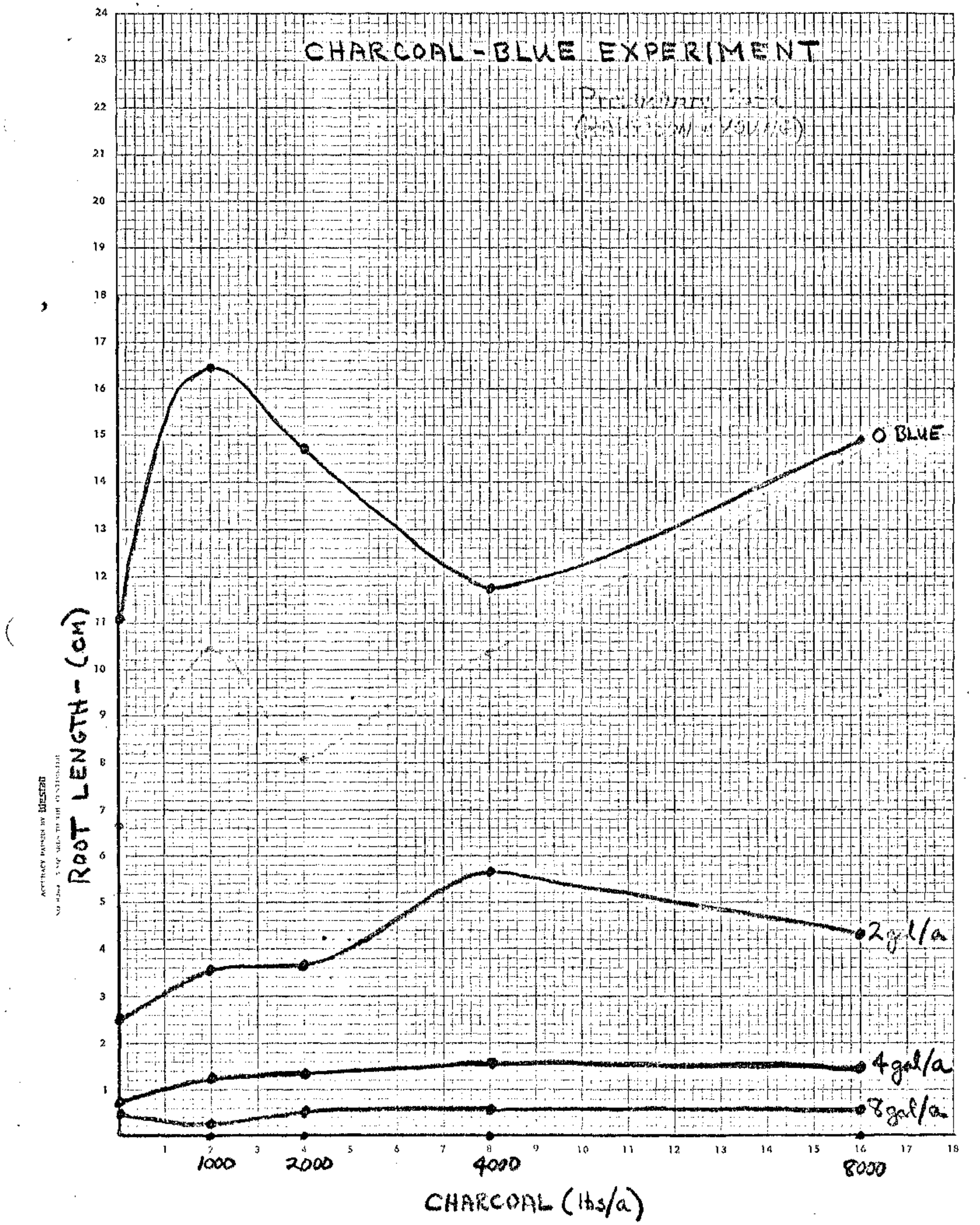
ORANGE

2,000 - 2 gallons.

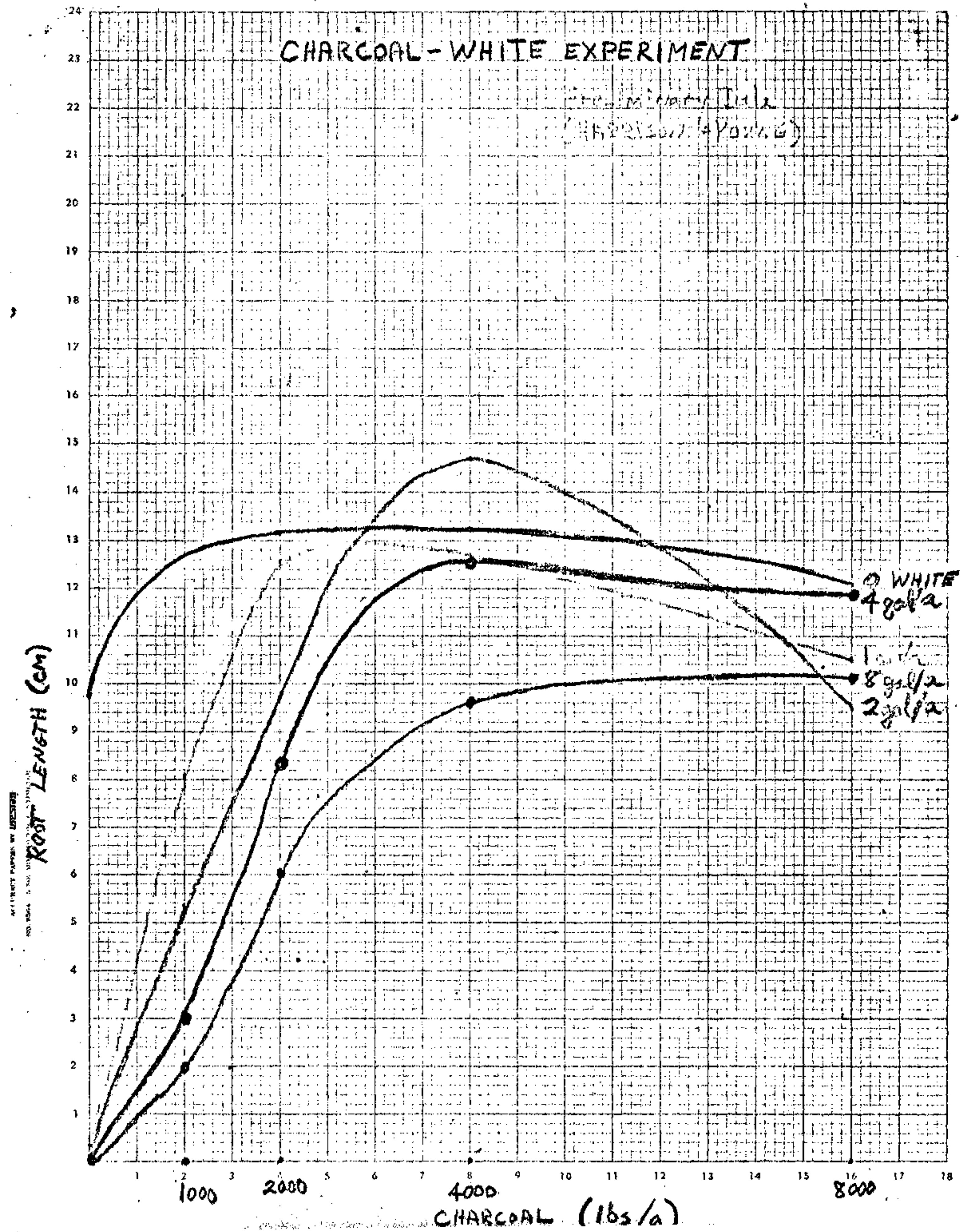
4,000 - 4 "

6000 - 8 "


CHARCOAL - ORANGE EXPERIMENT
Preliminary Data
(HARRISON + YOUNG)
ROOT LENGTH (CM)
8 gal/a
0 gal/a
4 gal/a
2 gal/a
1000
2000
4000
8000
CHARCOAL (lbs/a)



CHARCOAL - BLUE EXPERIMENT
0 BLUE
2 gal/a
4 gal/a
8 gal/a
ROOT LENGTH - (CM)
1000
2000
4000
8000
CHARCOAL (lbs/a)



CHARCOAL - WHITE EXPERIMENT
ROOT LENGTH (CM)
CHARCOAL (lbs/a)
1000
2000
4000
8000
0 WHITE
4 gal/a
8 gal/a
2 gal/a

For the aquatic / TCDD manuscript see.

Mullison, W.R. 1970 Effects of Herbicides on water and its inhabitants.

18(6): 738 – 750