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WASTE PESTICIDE MANAGEMENT

Environmental Health Sciences Center

Oregon State University

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NOTE: This is an informal report prepared by the investigators for limited circulation following a conference held on the above date on the Oregon State University Campus.

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Interim Progress Report

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INTRODUCTION

This program is involved in development of solutions to specific waste pesticide management problems. One of these activities, underway at Alkali Lake in eastern Oregon, involves field studies directed toward eventual safe disposition of approximately 1 1/4 million gallons of waste by-products of 2,4-D and MCPA synthesis which are currently in storage at this site. The other portion of the program consists of development of a system for management of spent pesticide containers accumulating in large numbers in one of Oregon's more concentrated agricultural centers.

Although these two waste management problems contrast rather markedly in terms of numbers of containers and volumes of toxic materials which must be managed, approaches to the problems have enough elements on commonality to warrant a coordinated research program. The basic problem in both these situations is to develop some method of rendering these toxic materials harmless, or at least compatible constituents with the environment. In degrading these chemicals, studies have been directed toward utilization of the same biophysical factors in the soil and other elements in the environment which degrade pesticides in the agricultural practice.

INDUSTRIAL PESTICIDE WASTE MANAGEMENT

Manufacturing Properties of 2,4-D and MCP

The phenoxy herbicides and, particularly, 2,4-D and MCP are well established pesticides for the control of weeds in agriculture. The plant growth regulating activity is primarily against broad-leafed plants at levels of 2 lbs/acre or less for many weed species.

Both MCP and 2,4-D are prepared by the same general reactions. The starting material for manufacture of MCP is o-cresol, or 2-methyl phenol, rather than phenol. The cresol is chlorinated to produce primarily 4-chlorocresol. However, as in the chlorination of phenols, other isomers are formed such as, small amounts of 6-chlorocresol and 4,6-dichlorocresol, in addition to the 4-chloro isomer. MCP is prepared by the condensation of 4-chlorocresol with chloroacetic acid.

In addition to the chlorinated phenols and cresols and chlorinated phenoxy acetic acids, there are some other polycyclic compounds in the waste material. These are formed by the condensation of the phenols under the hot alkaline conditions of the reaction mixture. If there is one point of attachment between rings, the resulting compound is an ether phenol. If there are two points of condensation, the resulting compound is a dioxin.

The dioxin formation was the cause for concern, initially, over the use of 2,4,5-T. 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. This compound is extremely toxic and elicits teratogenic effects.

Because of the nature of the starting materials, it is highly unlikely that any tetrachlorodioxin will be formed during synthesis of 2,4-D. However, since the dioxin is quite toxic, samples of 2,4-D waste were analyzed for its presence. The analyses were performed on a gas chromatograph attached to a mass spectrometer. Thus, it was possible to determine the nature of many of the impurities present in the waste, as well as the dioxin.

Analysis of this waste product indicated that there were no detectable amounts of tetrachlorodioxin or the trichloro derivative of dioxin. There was a small amount of dichlorodioxin present. This is what could be expected from the condensation of 2,4-dichlorophenol molecules. In addition, a number of other chlorinated compounds were also detected. The molecular weights of these compounds indicated them to be various isomers of chlorinated phenol-ethers.

The toxicity of these chemicals with respect to mammals is relatively low. LD₅₀ dosages range from 300 to 1,000 mg/kg body weight, depending on the species and sex of the animal tested. The LD₅₀ dosage for MCP in rats can be given as 700 mg/kg and, if this is extrapolated to man, the dosage would lie between 1.75 - 2 oz. of pesticide. On a similar basis, the LD₅₀ dosage for 2,4-D in man, would be in the order of 0.75 to 1 oz. By way of comparison, a single dose of about 1 oz. of aspirin is usually fatal. While these chemicals cannot be considered innocuous compounds in terms of drugs and other chemicals man commonly uses, they certainly are not considered highly toxic materials.

The primary reactions in the synthesis of these herbicides are essentially the same for both 2,4-D and MCP. The starting material in the manufacture of 2,4-D is phenol or carbolic acid, which is similar to the materials found in some common household disinfectants. The first step in the reaction is performed by chlorination of the phenol with chlorine gas. This process results in a number of isomers, depending on the location and number of chlorine atoms which become attached to the phenol ring. Thus, we can get 2- or 4-chlorophenol, 2,6-dichlorophenol or 2,4,6-trichlorophenol. By close control of the reaction, the primary product, however, will be the desired 2,4-dichlorophenol.

The second and final step in the formation of 2,4-D is the condensation, or coupling, of the 2,4-dichlorophenol with chloroacetic acid, a chlorinated derivative of acetic acid. In the manufacture of this compound, as in nearly all organic synthesis, all of the desired product cannot be recovered from the reaction mixture. Thus, the waste developed from the reaction contains 2,4-D, but in addition, it will also contain 2-chloro-, 4-chloro-, 2,6-dichloro-, and 2,4,6-trichlorophenoxy-acetic acid from the condensation of the by-product phenols with chloroacetic acid. There will also be the various chlorinated phenols that did not react to give the respective phenoxyacetic acids. Since the condensation reaction is carried out under alkaline conditions, the waste mixture will contain various phenols and phenoxyacetic acids as their sodium salts.

The only standard compound available for comparison to the constituents of the waste products was dichlorodioxin which was present at approximately 300 ppm. Toxicity of this compound is quite low compared with the tetrachloro isomer. In addition, it does not produce chloroacne in man, as does the tetrachloro isomer.

RATIONALE FOR BIOLOGICAL DEGRADATION OF PESTICIDE WASTES

There are many possible ways to handle the problem of chemical waste. In the past, non-destructive methods such as dilution in surface water and the ocean, or simple storage, have been widely used. Current concerns for environmental quality have resulted in standards which are no longer compatible with these approaches to management of the hazardous chemical wastes of our industry.

In order to effectively reduce the problem of management of hazardous chemicals, it is necessary to degrade or alter the toxic molecules through some type of chemical or biological degradation. The waste chemicals from production of phenoxy herbicides are relatively stable to chemical treatment. For this reason, chemical degradation would most reasonably be accomplished by oxidation through incineration. This method is complicated, however, because most incinerators have the potential for contribution to air pollution.

At least until sophisticated incineration or pyrolysis techniques become technically and economically feasible, the alternative of biological degradation holds considerable promise. This is certainly not a new concept, since we rely on the process of microbiological degradation to prevent build-up of pesticides used in crop production. The primary difference between agricultural use and a chemical waste management operation lies in the amount of chemical applied. Obviously, much larger amounts of chemical would have to be involved in a feasible chemical waste management operation.

In order to use soil as a receptacle of waste chemicals, two primary criteria must be met. The first is that the soil microorganisms must be able to degrade the chemical wastes to environmentally acceptable entities at relatively high rates of waste application. This means that the soil microorganisms must not be inhibited by the waste and they must be able to decompose the waste components. The second criterion is that the characteristics of the site of application of waste materials must have a minimum potential for the chemicals leaving the site in any way or form that would result in their becoming environmental pollutants.

Nearly all organic pesticides have been shown to be degraded in soil when applied at normal rates of application. The extent of soil life varies from a few days to several years with the more persistent materials. It is known that the phenoxyacetic herbicides do not persist from one growing season to the next, when used in normal agricultural rates. The primary route of loss of pesticides is considered to be microbiological rather than chemical in nature. The microbiological nature of the decomposition is indicated by: 1) Soil and climatic factors that are conducive to high microbiological activity result in the most rapid rates of decomposition. 2) The rate of herbicide decomposition in biologically sterile soils is greatly inhibited. 3) There is a "lag" period before herbicides in soil begin to decompose.

This lag period is considered to be due to adaptation of the microorganism populations to the chemical or to the time required to build a population of species of organisms which are capable of decomposition of the constituents of the pesticide. After this lag period, there is a relatively rapid decomposition of chemical. This adaptation to the chemical may consist of induction of enzyme systems capable of utilizing the chemical as a carbon source, or some other energy source, or to selective enrichment of the soil, with respect to the organisms that are already present in the soil and capable of metabolizing the herbicide. In any event, after the soil is enriched, subsequent additions of the chemical persist for a much shorter interval of time.

A survey of the literature indicates 2,4-D persists no more than a few weeks and MCPA up to three months following application at normal use rates. Subsequent additions of the chemical, in the course of management of weed populations, frequently result in residues of only a few days duration. There also appears to be evidence of an inter-relationship in the response of microorganisms to both 2,4-D and to MCP. Thus, after soil has gone through a lag phase of enrichment by 2,4-D, there is no corresponding lag period where MCP has subsequently been used. The reverse also appears to be true where MCP is first employed. These facts certainly appear to favor utilization of soil for repeated applications of phenoxyacetic waste materials.

The mechanism of phenoxy acid degradation involves cleavage of the ether substitute and hydroxylation of the ring. Ether cleavage of the ring produces 2,4-dichlorophenol, which is also present in the 2,4-D waste material. The 2,4-dichlorophenol is hydroxylated and, subsequently, the ring is opened with the result that there is little chance of toxic or persistent metabolites resulting from microbial metabolism of 2,4-D or dichlorophenol.

An important consideration in biodegradation of chemical wastes is the effect of the waste upon the microorganisms. All the available literature indicate that there is no inhibitory effect of 2,4-D on microorganisms at normal rates of application. At high rates, the effect is variable, depending upon the species of organisms. Certain species are reported stimulated by as much as 1000 ppm of 2,4-D in the soil. It is reasonable to expect that many organisms can adapt to the chemical and utilize it at least as a carbon source.

With these concepts in mind, we proceeded with some bench scale studies to determine the ability of soil from the Alkali Lake site to metabolize the 2,4-D waste. Soil was treated with approximately 100 ppm 2,4-D and analyzed periodically

to determine the amounts residual. The results of this study agreed with those of other investigations of rates of degradation of 2,4-D in soil. In soil from two areas of the test site, there were lag periods of from 8-13 weeks before the chemical started degrading. After this time, there was rapid degradation resulting in complete loss of the chemical. Subsequent to these initial observations, test plots were then established to determine the rate of 2,4-D and dichlorophenol degradation under actual field conditions at the Alkali Lake test site.

BIODEGRADATION STUDIES AT ALKALI LAKE

Studies on the use of soils surrounding Alkali Lake in Lake County, Oregon, for biodegradation of industrial waste derived from production of 2,4-D and other phenoxy herbicides have matured to a point permitting a comprehensive, but not final, report.

Alkali Lake Site Physical Features:

The Alkali Lake site consists of an alkaline playa of approximately 3500 acres and land immediately surrounding; bring the total holding to approximately 6000 acres. The playa constitutes a base level for surface drainage within a closed basin approximately 300 square miles in area. The Alkali Lake basin was the site of an ancient lake, some 20,000 years ago, so that the playa has been the terminus of regional drainage at least for that length of time. The disappearance of the ancient lake is considered to be the result of climatic changes rather than due to breaching of restraining rock formations. Faulting and tilting of rock units in the Alkali Lake vicinity are thought to form surface barriers to movement of deep ground waters.

The Alkali Lake area has been the subject of geological investigation for many years because of interest in potential mineral resources. Most recent investigations have been undertaken by the Oregon Department of Geology and Mineral Industries, in connection with the current studies evaluating the use of the site for management and degradation of specific chemical wastes. The results of these studies are available in an Open File Report prepared by this agency entitled, "Geologic Evaluation of the Alkali Lake Disposal Site". These studies determine that the north end of the property adjacent to the playa is unsuitable for use because sediments are porous near the surface and a considerable amount shallow subsurface drainage was entering the basin at that end. Sediments on the land adjacent to the southern portion of the playa were found to be less porous and associated ground water was very salty, stagnant and lay at a much greater depth. This portion of the property was judged to be more suitable for establishment of a biodegradation program.

A brine pool was found to underlie the present dry lake extending to a depth of more than 100 feet, but with diminishing salt content below 40 feet. Fresh water occurs approximately 130 feet below the lake basin on the north end and at 260 feet on the south end. This fresh water zone is separated from the saline waters of the lake by 50-100 feet of impermeable rock. There are deep artesian wells at the north and south ends of the lake which flow fresh water and there are several springs seeping out at the surface on the north and west sides of the playa.

The playa evaporites in the brine pool contain high concentrations of arsenic. The springs found seeping around the lake also contain high concen-

FIG. 1. Some of nearly 25,000 drums of chemical waste from 2,4-D and MCPA manufacture in storage at Alkali Lake.

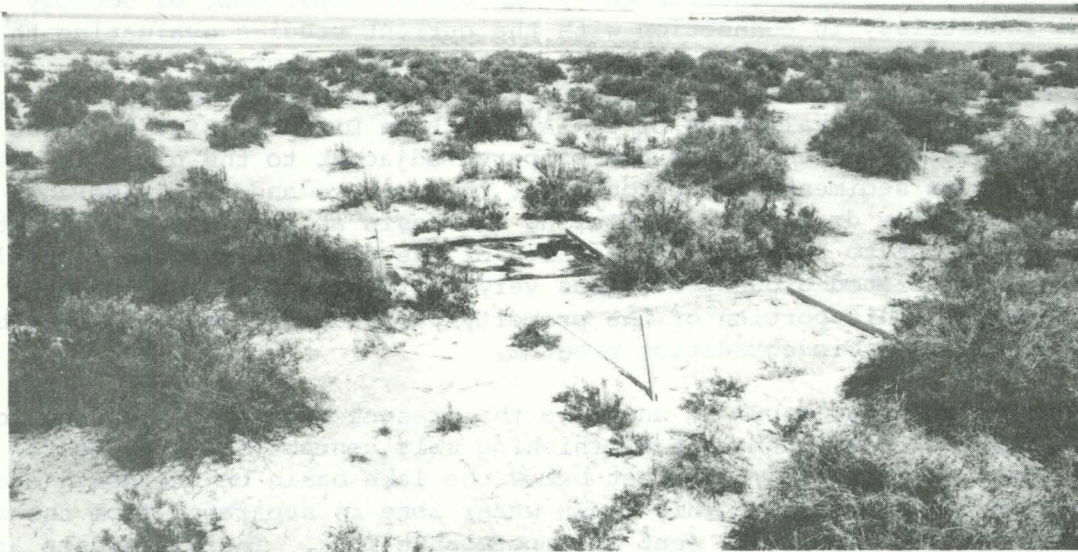
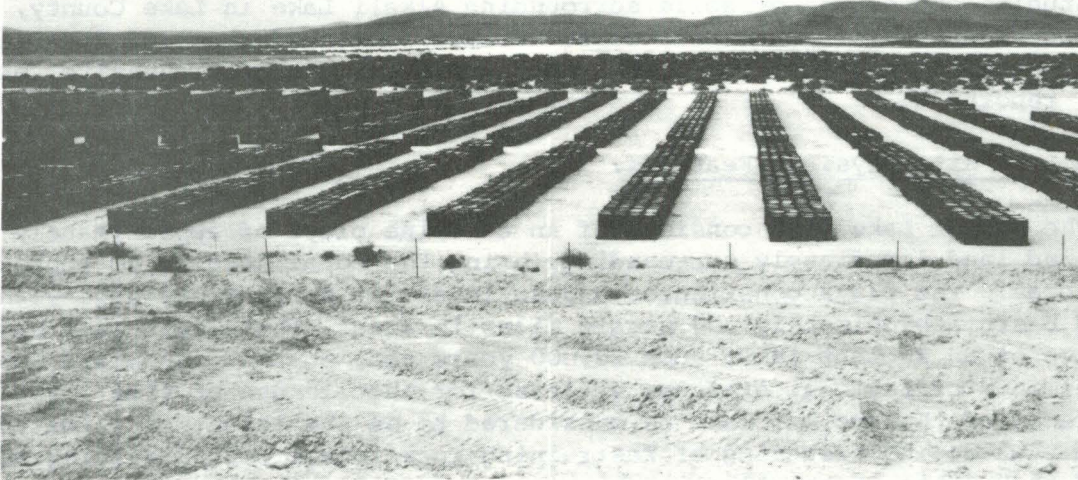


FIG. 2. Small plots with and without plastic covers. Note sparse vegetative cover typical of area.

trations of arsenic except the large spring on the north side of the lake which flows fresh water with only a trace of arsenic. This spring is believed to be connected to the deep fresh water aquifer. Analysis of water from the two wells showed high arsenic content but this may be due to mixing with saline waters during ascent through the well bores. Water movement, both surface and subsurface, is directed into the basin.

Alkali Lake basin is judged on basis of geologic evaluation to meet the requirements for disposal of waste chemicals since: a) the site is remote b) land has a low-use potential, c) water resources will not be contaminated.

Disposal of chemicals, however, should be confined to the southern half of the property on the basis of geologic studies to date. Addition of chemicals directly to the playa or to the underlying brine pool, is considered to be undesirable. Neutralization or alkaline degradation of the chemical waste should be accomplished on higher ground without contact with naturally occurring surface of subsurface water which drains into the playa.

The western quadrant of the lake shows evidence of the extensive wind erosion which has been a predominant feature in the development of the modern Alkali Lake. At least 30 feet of the original lake bed sediments have been removed by this means since the original lake disappeared. The weather is typical of the arid semi-desert of eastern Oregon with temperature extremes in excess of 100°F in the summer to subzero occasionally during the winter. The soil commonly freezes to a depth of from 3-6 inches. Annual precipitation varies from 6-12 inches and an annual evaporation rate of in excess of 70 inches prevents any appreciable accumulation of water on the alkaline playa surface.

Small Plot Studies - Preliminary

The initial segment of the program to assess the potential of these alkaline soils for biodegradation of the phenolic wastes and herbicide residuals was conducted in a series of small 10' X 10' plots. Plots of this size were selected in order to minimize any unexpected impact on this environment in the event unfavorable reactions developed following reduction of the waste material.

Initial tests were concerned with the possibility of vertical movement of the pesticide in the soil following addition of water. Approximately six inches of water, equal to two-thirds of the annual rainfall, were applied to plots treated with waste at a rate equivalent to 300 lbs. of 2,4-D per acre. Soil samples were taken on these plots and in all subsequent plots by means of a three-inch soil auger. The soil profile was sampled in increments so that vertical distribution of the waste could be ascertained. This sampling procedure was continued in all the subsequent small plots studied. Samples were then returned to the laboratory where they were extracted and analyzed for 2,4-D and dichlorophenol content expressed in terms of ppm of soil.

The data summarized in Table 1, represent a comparison between a plot receiving the normal annual rainfall and a plot flooded with a total of six inches of water immediately following treatment and then exposed subsequently to the normal rainfall of the region. The data appearing in Table 1 represent a summary of eight sampling intervals over a period of a little more than one year expressed as an average concentration per unit inch of profile segment.

Table 1.

Distribution of DCP Bleed Waste in Soil
300 lb/Acre 2,4-D Equivalent Surface Application

	PPM per unit inch of Soil Profile Segment							
	0-2"		2-6"		6-12"		12-18"	
	2,4-D	DCP	2,4-D	DCP	2,4-D	DCP	2,4-D	DCP
Normal Annual Precipitation	92	85	5	7	2	7	1	1
Normal Pptn and Flooding to 6"	5	28	20	12	34	31	41	29

It can be seen that where flooding did not occur, the concentration of waste material, in terms of 2,4-D and DCP, remained at, or very near, the surface of the soil. Flooding contributed immediately to a vertical distribution into the lower depths of the soil which was retained throughout the one-year interval of observation. These observations indicate that while this waste may be highly mobile, under conditions of flooding, or high rainfall, that the more normal annual precipitation results in minimal vertical movement. The data also suggest that use of intensive irrigation to promote more rapid biodegradation or to support a cover crop may be contra-indicated.

In addition to the observations on vertical movement, subsequent small plot studies involving material applied to narrow trenches also indicated very little horizontal movement beneath the surface of the soil. In summary, these observations indicate essentially no migration of the waste in the soil once it has been applied; unless excessive water is added.

Particulate Transport and Movement of Volatiles:

Although there appear to be a rather minimal chance of migration of the waste chemical within the soil, the wind erosion occurring in the area clearly indicated the likelihood of particulate transport from soils subject to surface application. Additionally, it is also perfectly obvious to those working the small plots that a volatile fraction is continually being removed from soil receiving surface applications.

Observations were initiated to determine the significance of movement of components of the waste material on particles, or as a volatile fraction in the air. Five 2' X 2' glasswool filters were installed around the vicinity of the experimental area and the drum storage area, in what was normally down-wind exposure. Initial observations indicated no detectable levels of 2,4-D on short-term exposure of one week or less, in any of the filters. Subsequently, exposure was carried out between the interval of 12 May and 15 July, or nearly two months. Amounts of 2,4-D accumulated in these 2' X 2' glass filters are summarized in Table 2.

Table 2.

PARTICULATE TRANSPORT
2' X 2' Glasswool Filters, Exposed 12 May-15 July, 1970

<u>Location</u>	<u>μ 2,4-D</u>
100 yds SE of Drum Storage	80
300 yds NE of Drum Storage	28
800 yds NE of Drum Storage	3
50 yds SE of Small Plot Area	83
100 yds SE of Small Plot Area	40

Based upon this small number of collection stations, a mid-point concentration of 2,4-D at 400 yds. appears to be in the order of 20 μg/4 sq. ft. of filter surface. An extrapolation from this, in terms of pounds per acre, would be in the range of .002 lbs. of 2,4-D/acre deposited over a two-months' interval across the full 800 yards downwind from the source sites. This represents a 2,4-D exposure of about .0001 - .0002 of the usual single 2,4-D application for control of undesirable range plants in this portion of eastern Oregon.

Air samples have been collected on two occasions during the summer months over the surface of the small plots, as well as within the drum storage area. Two Gelman microimpingers, connected in series containing ethylene glycol, were used as a collection system. Air was bubbled through this system at a rate of one liter per minute for intervals up to six hours without detection of chlorinated phenols. Calibration in the laboratory indicated the sensitivity of the method to be in the order of 7 ppb. The odor of chlorinated phenols in the air at the time the samples were taken was perfectly obvious, indicating that concentrations of phenols were relatively small and that the human olfactory threshold was also in very low order of magnitude.

Small Plot Studies

The primary series of small plots were set up to determine rates of degradation of 2,4-D waste. Results of these plot studies are summarized in the figures which follow in terms of ppm 2,4-D or Dichlorophenol per unit inch soil profile over the entire depth of 0-18 inches. With a few exceptions, samples were taken at 6-8 week intervals, over a period of a little more than 600 days.

It should be borne in mind while interpreting the figures which follow, that the expression, ppm 2,4-D or DCP/unit inch of soil profile is, in effect, an average of concentrations along the profile and that much higher values will occur at the original point of the deposit of the waste material as exemplified in Table 1.

The hypothetical degradation curve referred to in a previous section of this report, is represented in Figure 3. Its principle features are an initial lag period representing an interval of microbiological adjustment followed by relatively precipitous decline in concentration of the chemical. As concentrations of the chemical diminish, the rate of degradation attenuates as the biological activity again readjusts to reduced concentrations of the agent. The lag period is not

Fig. 3
HYPOTHETICAL DEGRADATION CURVE

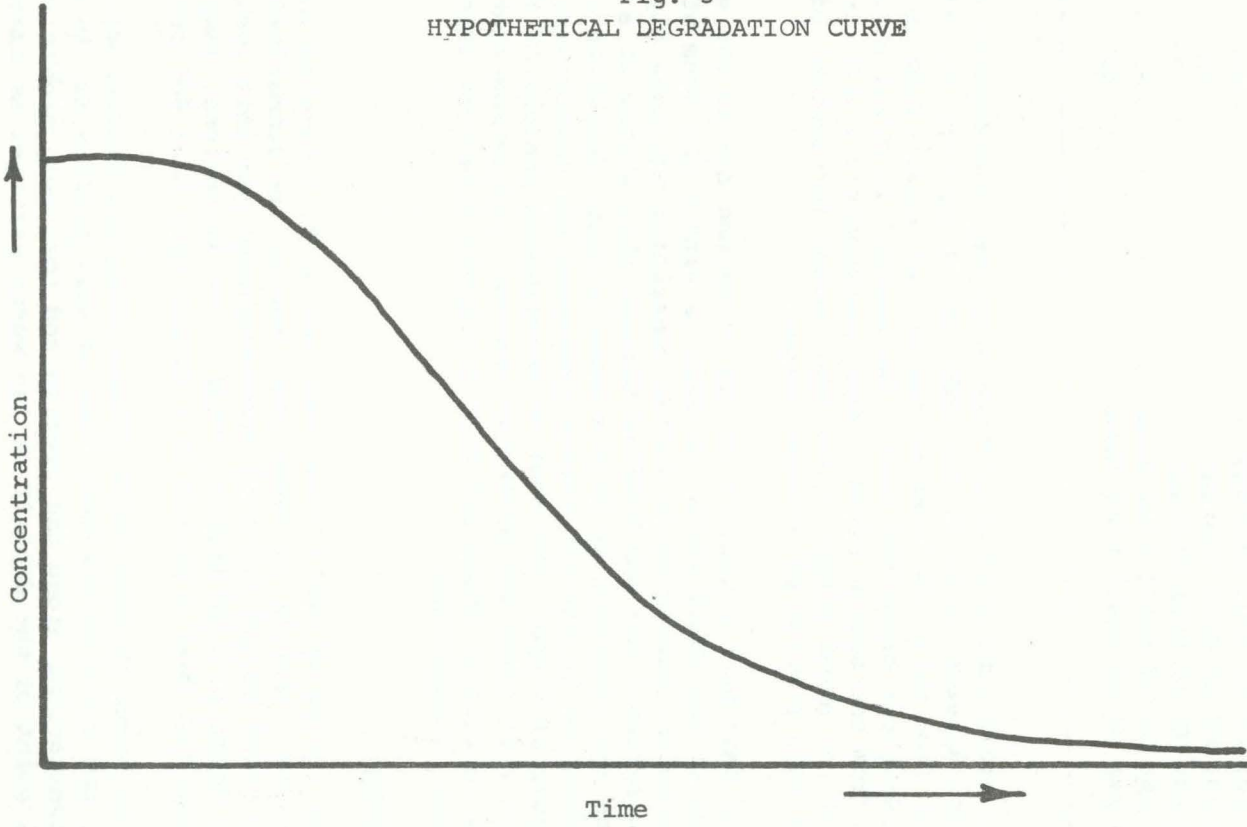


Fig. 4
SURFACE APPLICATIONS
2,4-D Fraction

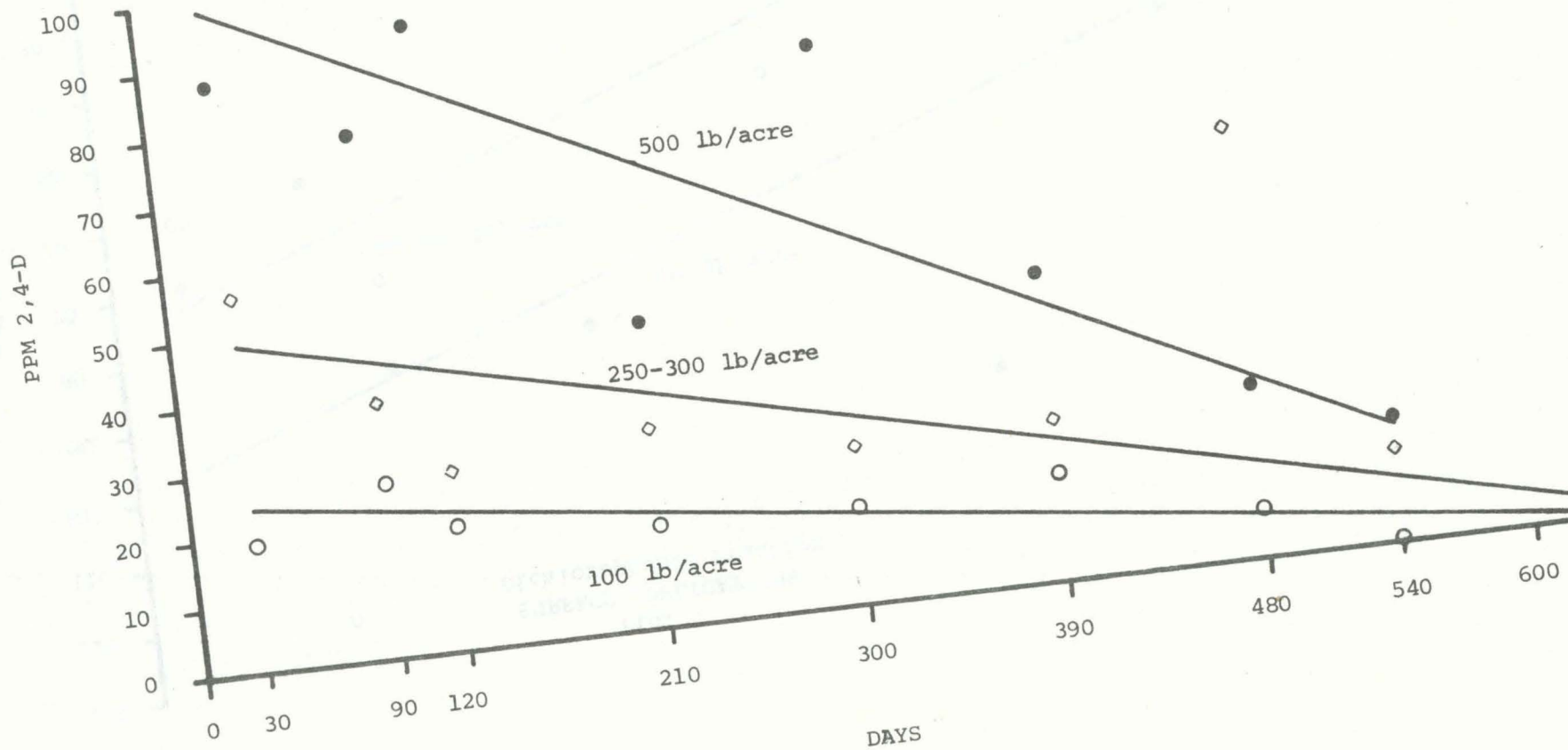
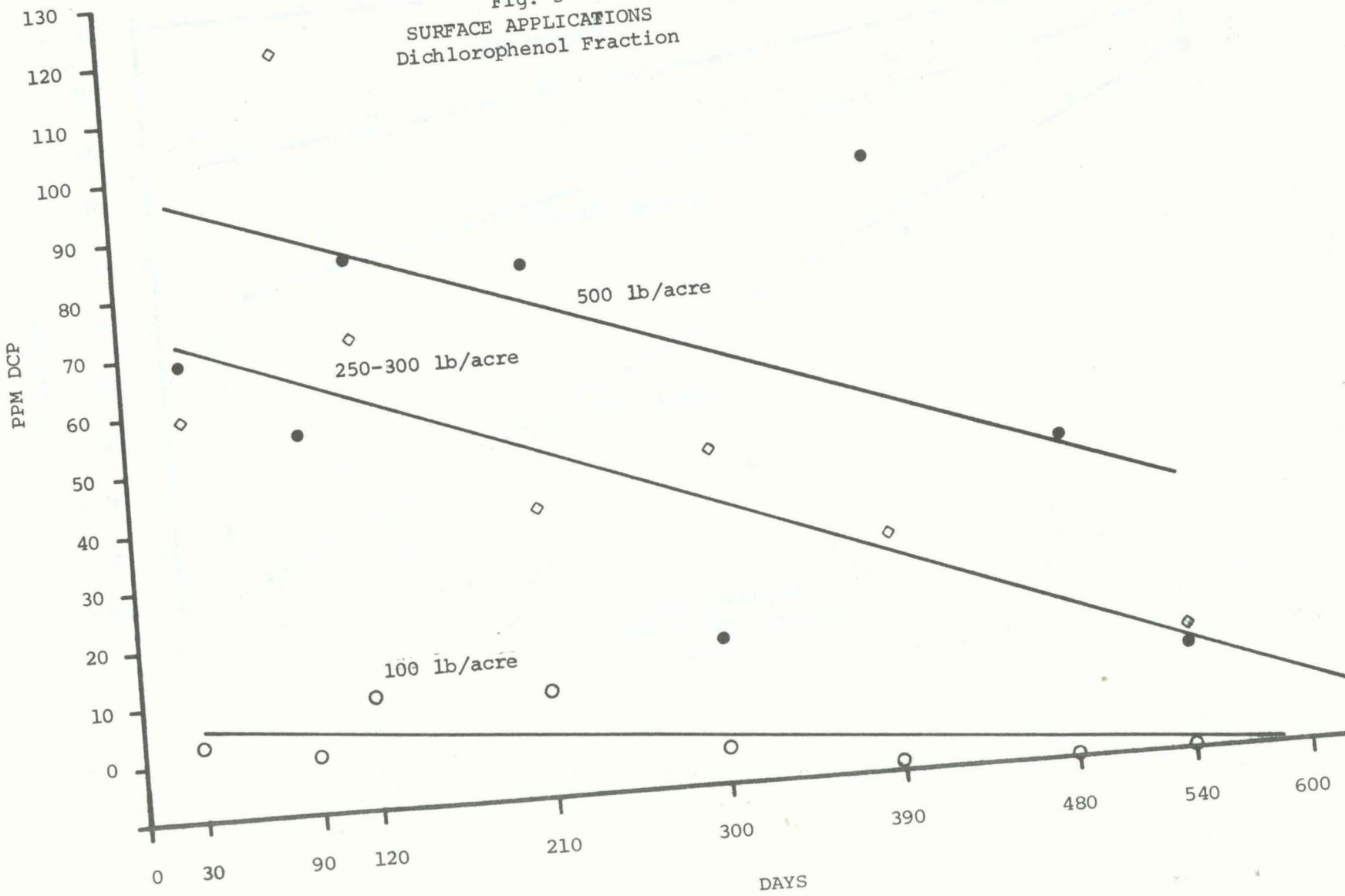
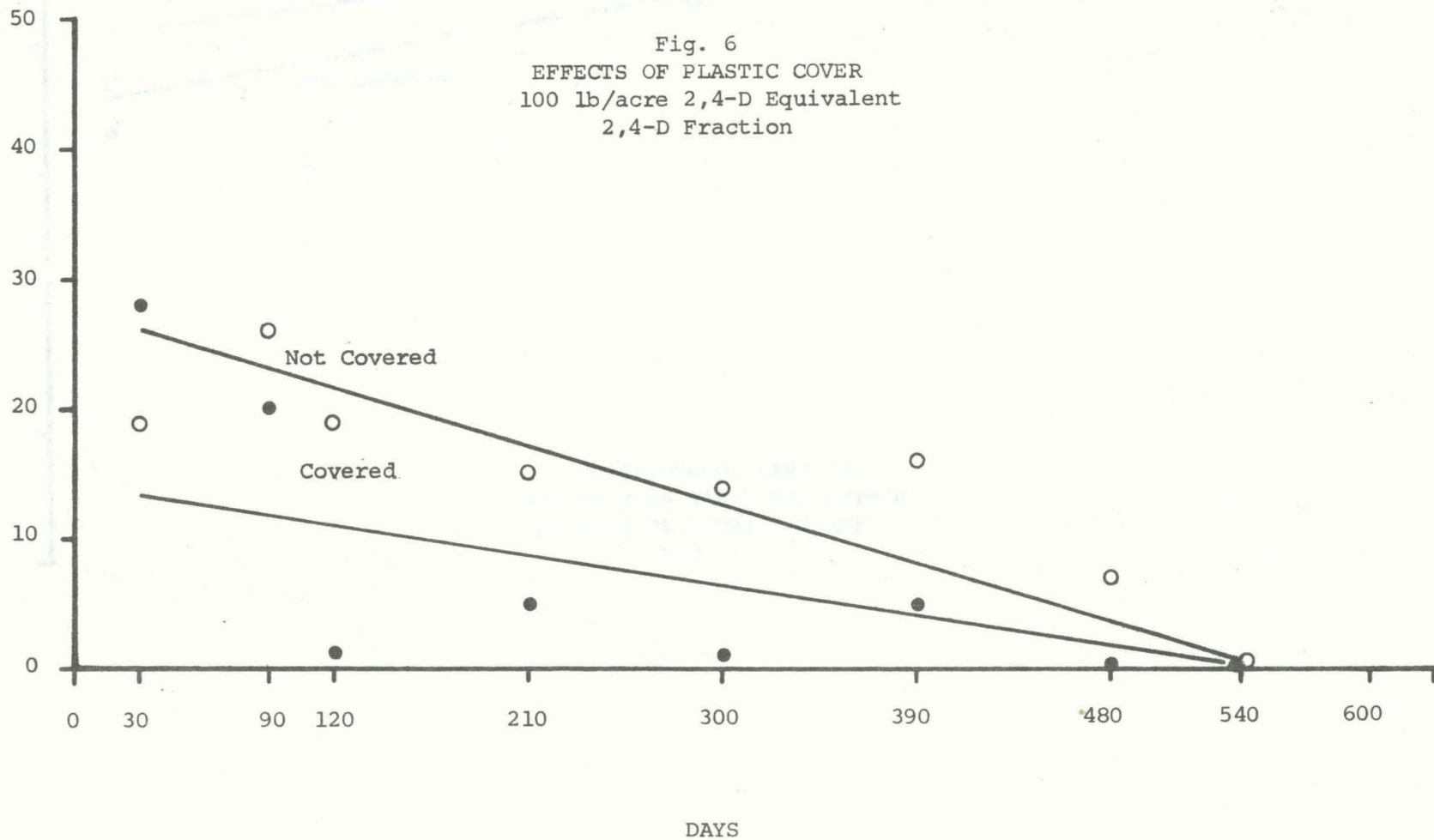


Fig. 5
SURFACE APPLICATIONS
Dichlorophenol Fraction



PPM 2,4-D



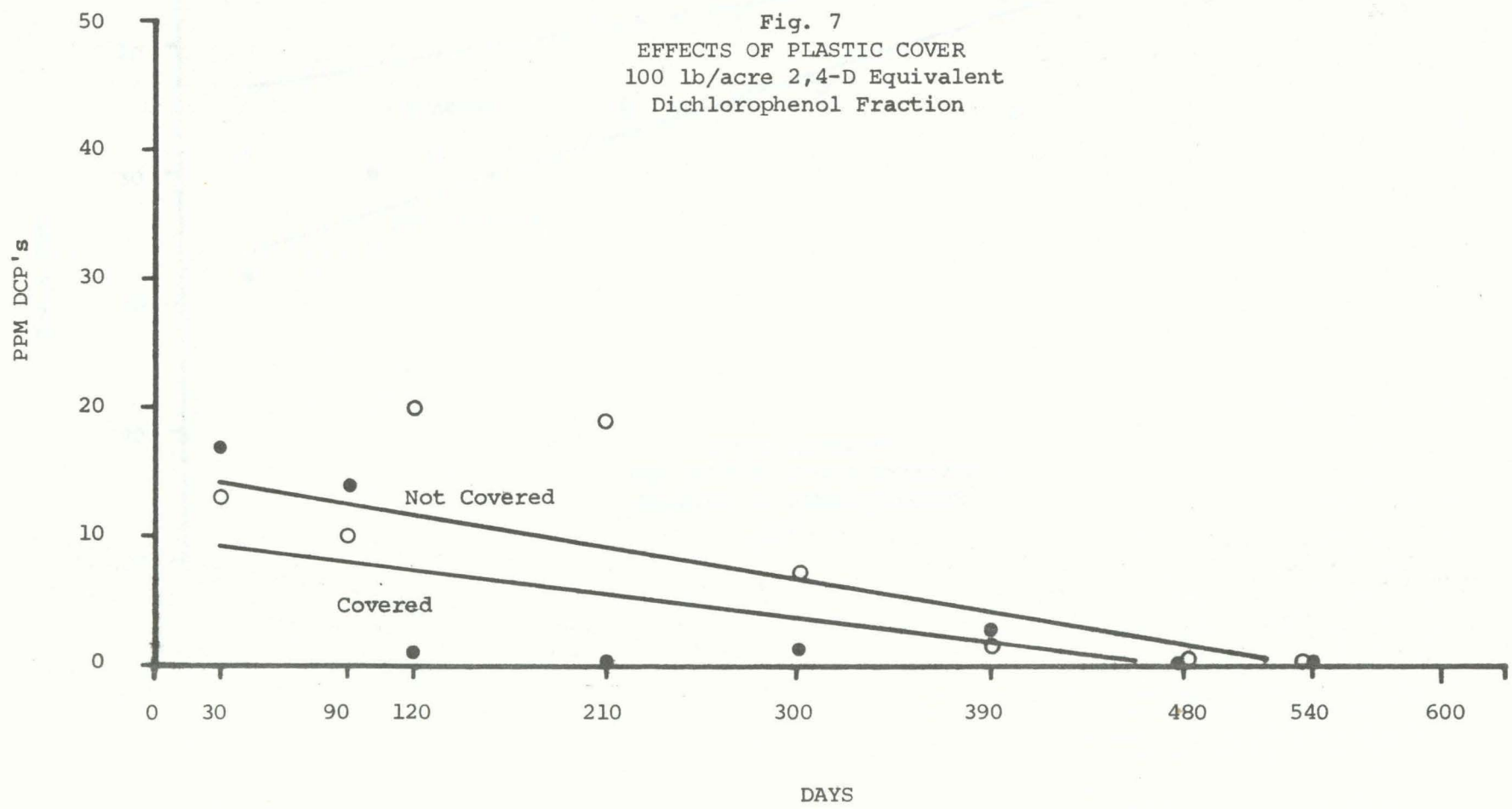
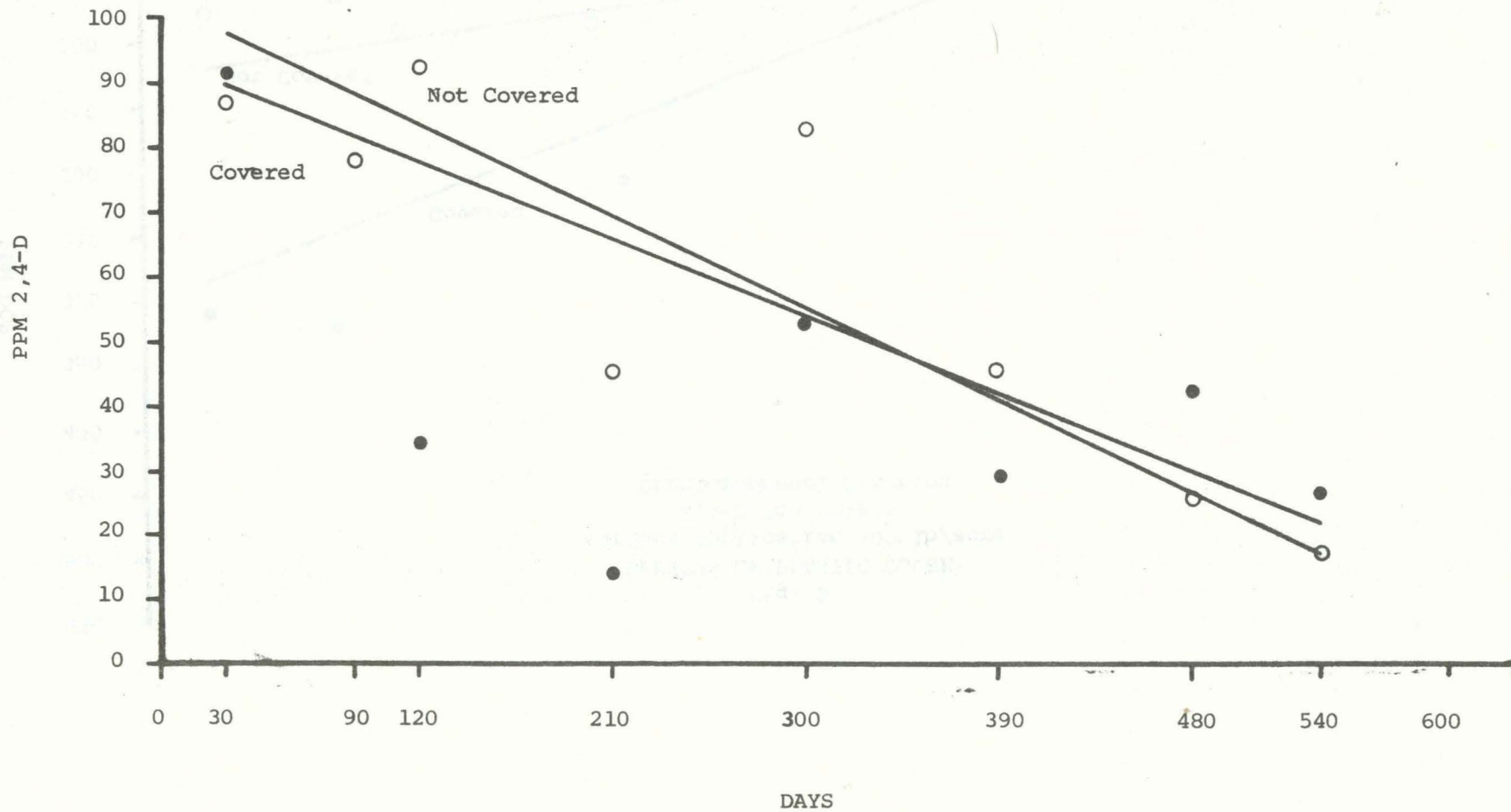
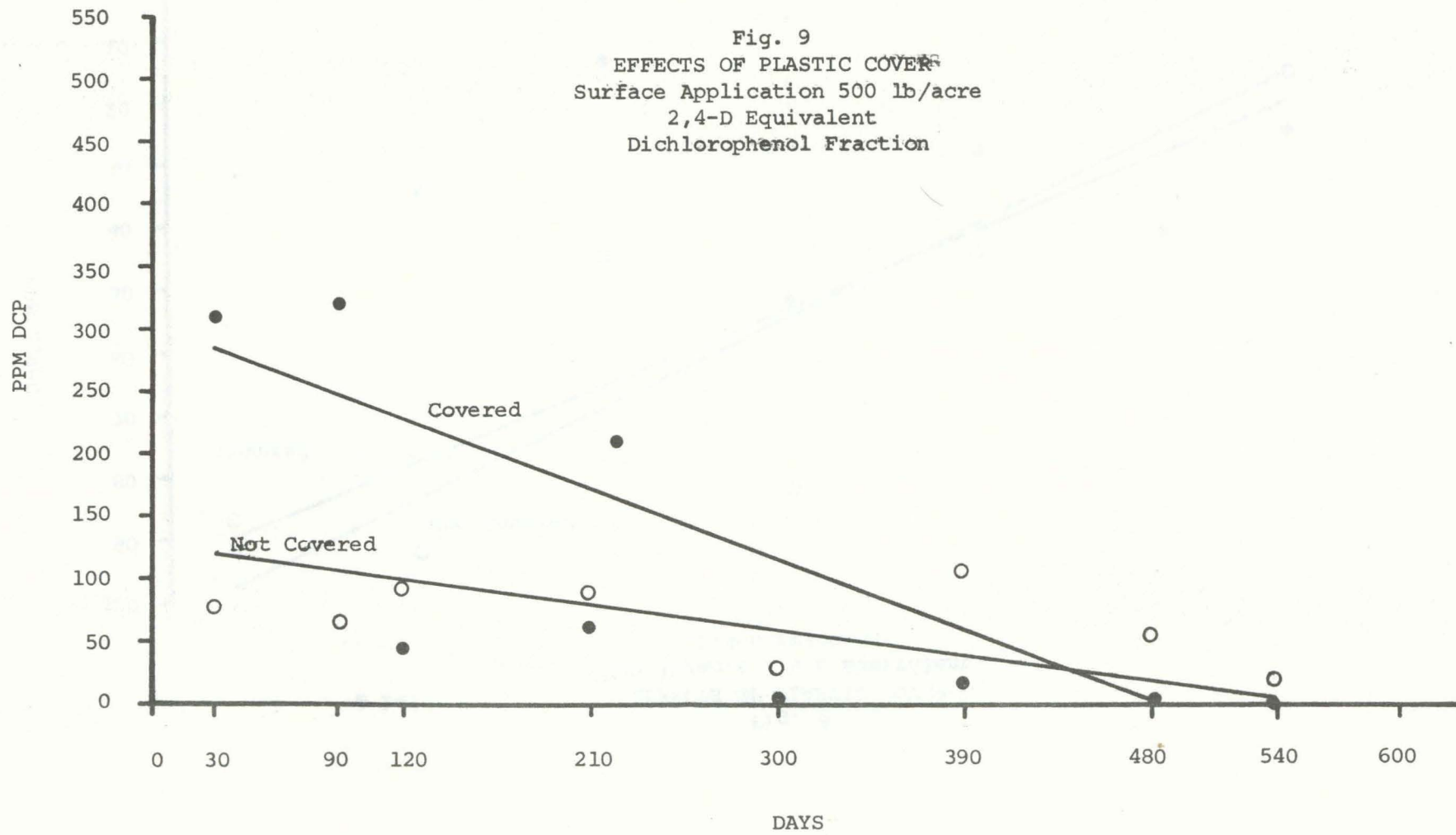


Fig. 8
EFFECTS OF PLASTIC COVERING
500 lb/acre 2,4-D Equivalent
2,4-D Fraction

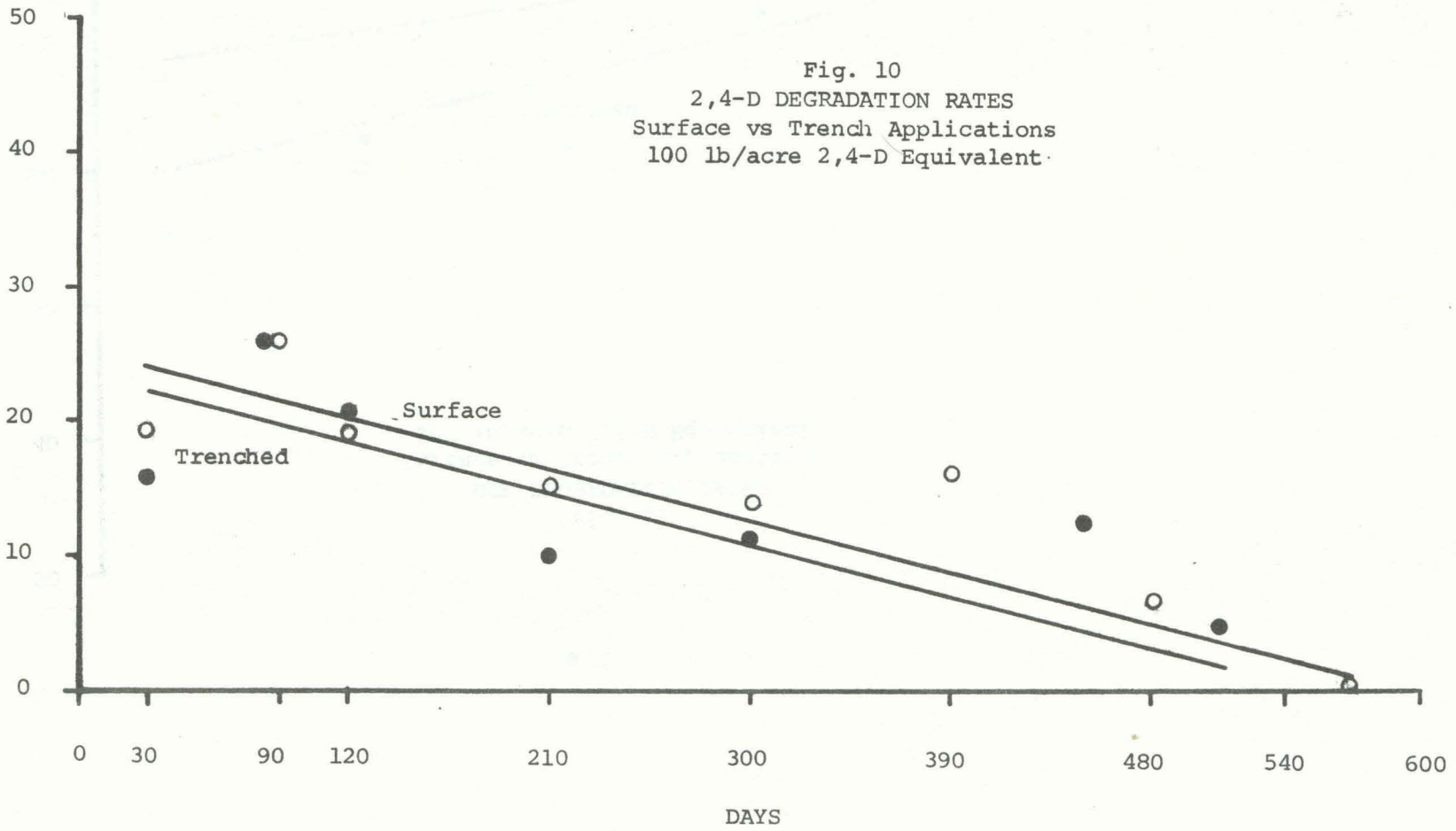


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Fig. 9
EFFECTS OF PLASTIC COVER
Surface Application 500 lb/acre
2,4-D Equivalent
Dichlorophenol Fraction



PPM 2,4-D



PPM DCP

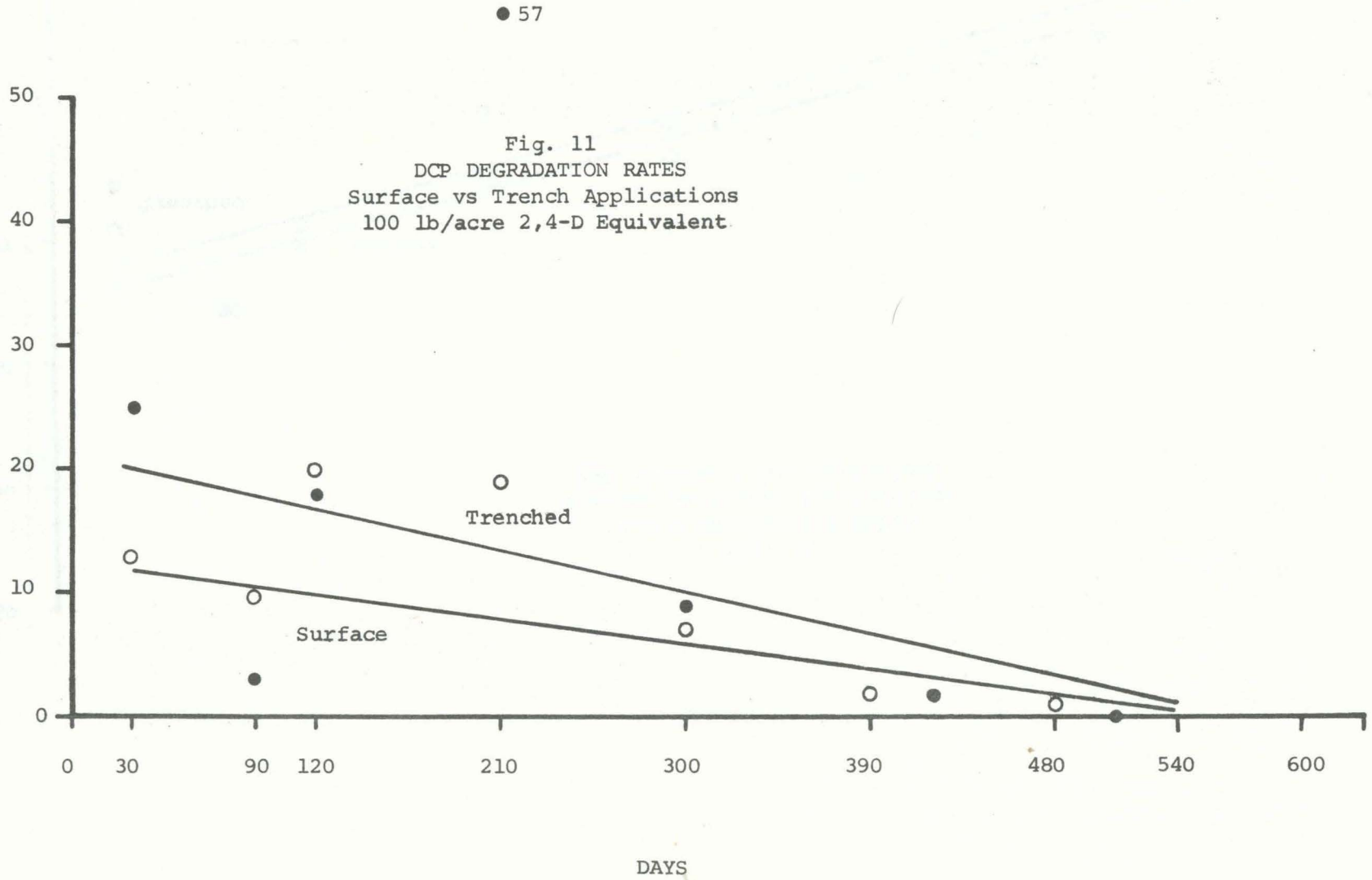


Fig. 12
2,4-D DEGRADATION RATES
Surface vs Trench Applications
500 lb/acre 2,4-D Equivalent

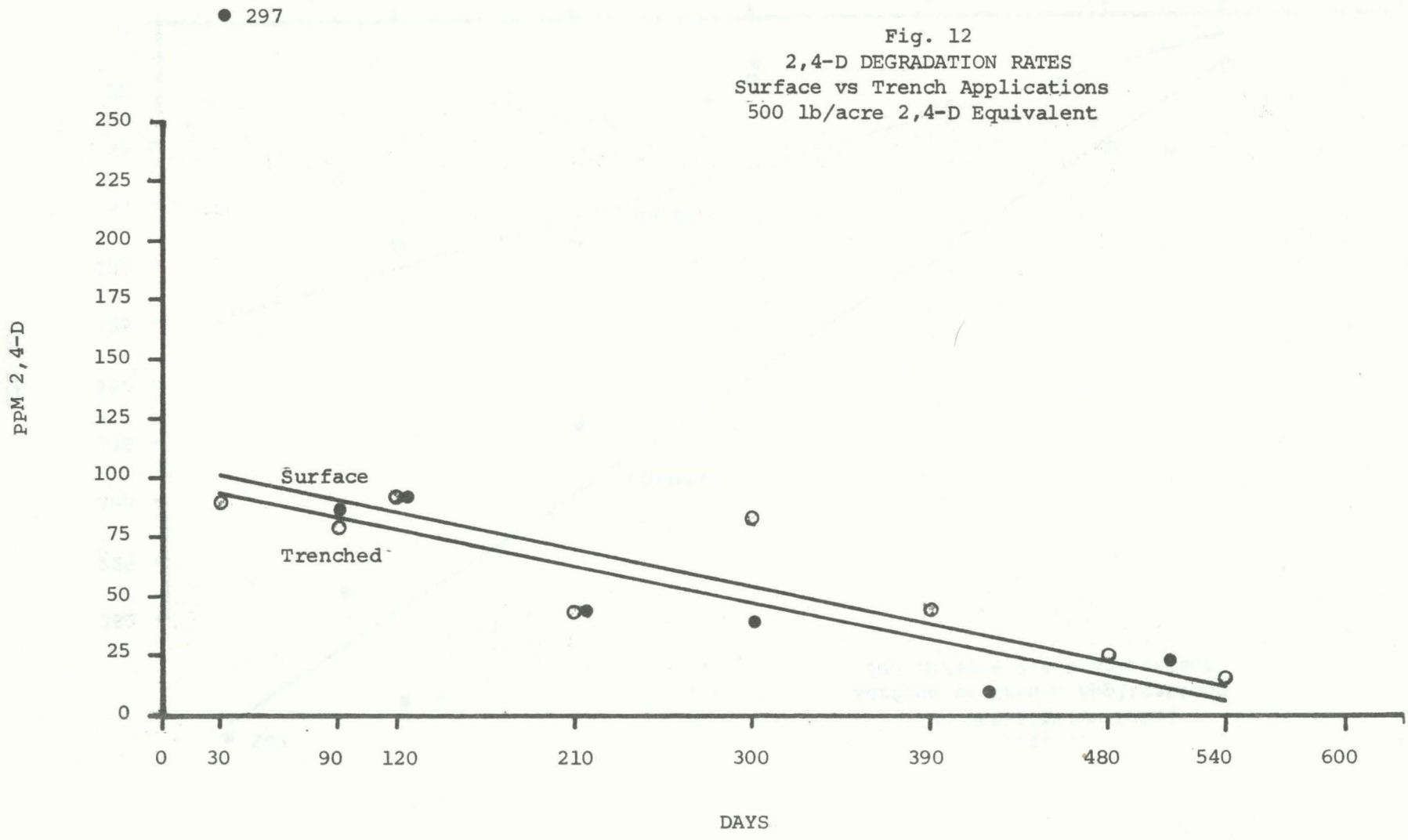
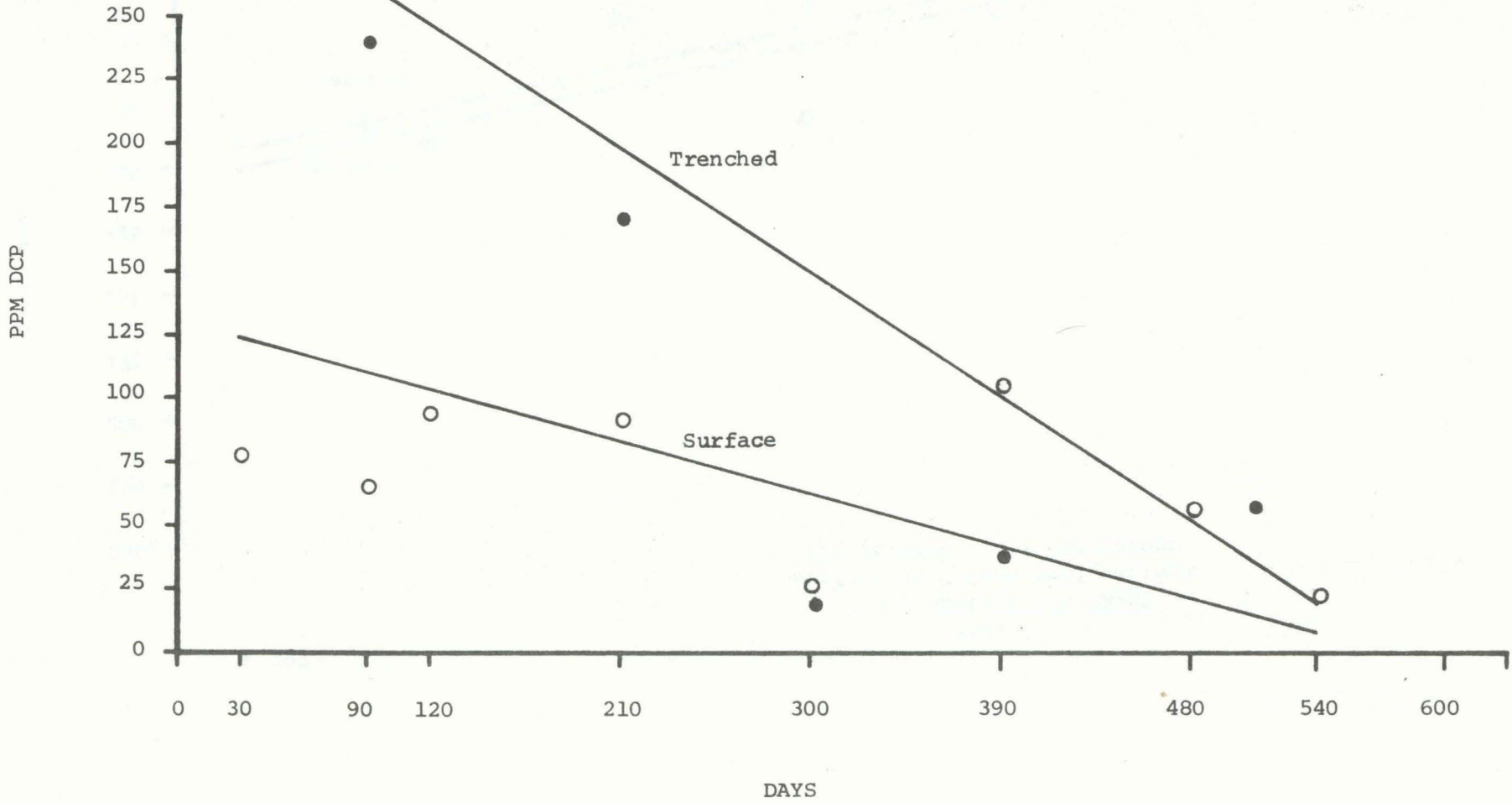


Fig. 13
DCP DEGRADATION RATES
Surface vs Trench Applications
500 lb/acre 2,4-D Equivalent



clearly evident in the data developed in the small plot studies; however, there does appear to be a well defined decline. Seasonal variation in soil characteristics affecting the soil sampling program and uneven distribution of the chemical have contributed to a good deal of scatter in the analytical values resulting from these tests.

Results of surface applications of the waste material at rates varying from 100-500 lbs/acre 2,4-D equivalent are illustrated in Figures 4 and 5. These data indicate a clearly apparent degradation of the 2,4-D and dichlorophenol fractions over an interval of more than 600 days. Scatter in the DCP data at the 500 lb. dosage was extreme and, although an attempt was made to fit a line, it is of doubtful validity. The best that can be said of this data is that there is an apparent decline. Other than this discrepancy, all dosages and both fractions indicate a rather clear degradation which is apparently dosage independent within the dosage ranges employed. Similar observations have been reported in agricultural usages of herbicides where, of course, dosages were much lower. It would appear likely that within some as yet unattained dosage threshold, once microbiological activity has become adjusted for presence of the waste, that rate of degradation approximates first-order kinetics and, thus, is independent of the concentration of material present.

Because of concern for the possibility of removal of the waste material on windblown particles, small plot experiments were set up to determine the effects of covering the surface of the soil with black plastic. Results of these experiments are illustrated in Figures 6 through 9, where waste was applied at the rate of 100 and 500 lbs/acre 2,4-D equivalent, and immediately covered with a black polyethylene film. Throughout the more than 600 day interval of observation, it was noted that not only did the plastic prevent particulate removal, but also that the volatile component so readily detectable on the 500 lb/acre plots not covered, was not detectable as an odor above these plastic covered plots. Additionally, the plastic served as an effective moisture barrier so that the soil surface remained relatively moist throughout the interval of exposure in contrast to the very dry state of the soil during the hot, arid portions of the year in the surrounding terrain. Although the plastic was beneficial in terms of limiting removal of the waste chemical from the soil surface, the data as summarized in the accompanying figures indicate little, if any, advantage in terms of acceleration in rate of degradation. This approach may also be valuable as a means of preventing surface run-off during intervals of high rainfall and might be considered as an option in planning other chemical waste biodegradation projects where higher rainfall may be an important consideration.

As a more practical and less expensive alternative to the plastic cover in controlling airborne transport of waste material, studies were initiated on the effects of application of the waste in trenches approximately 10" below the ground and set on two-foot intervals. The results of this series of experiments are summarized in Figures 10 through 13. It was considered that these trenched plots would essentially simulate subsurface injection of material as a practical scale operation. The net effect of the application differs from surface applications in that the material is concentrated in bands approximately 5" wide, instead of being more or less uniformly distributed across the surface of the plot. Thus, where applications of 100 and 500 lbs/acre 2,4-D equivalent were made in 5" bands on two-foot centers, the actual concentration of material within these bands was approximately five times that of the surface application. Samples taken between trenches and in soil profile segments from the surface down through the point of application, indicate minimal vertical and horizontal movement of the agent from the site of initial deposition.

Under these conditions, with a relatively high concentration at a depth of about 10" beneath the surface of the soil, it was encouraging to note relatively little difference in the rates of degradation in the trenched plots and the surface applications. In Figure 13, the DCP degradation rates at 500 lbs/acre 2,4-D equivalent are badly scattered for both the trenched and the surface applications. Apparently, however, the averaging effect of determining concentration in terms of ppm per unit inch of soil profile still reflects a very high concentration of DCP at the 6-12" segment of the soil profile. The rather sizable variability in analytical data preclude a more detailed analysis of this difference. In any case, values beyond 300 days indicate that there was marked diminution in dichlorophenol in samples drawn within the trenches.

In addition to analyzing the soil samples for concentrations of 2,4-D and chlorophenol, a microbiological examination of these same samples from small plots was also conducted. Cultures were made on media at both pH7 and pH10, and in addition to plate counts, notation was also made of the relative numbers of bacteria, actinomycetes, nocardial organisms and fungi. Plate counts at both pH7 and pH10 indicated both seasonal effects and possibly an effect of the waste material on numbers of organisms. Relative quantities of the groups of microorganisms did not vary enough to indicate any major qualitative shifts in the population following introduction of the waste chemical.

SUBSURFACE INJECTION

The final series of tests covered by this report deal with 1/8 acre pilot scale subsurface injection plots. Two plots were applied by means of tractor-drawn equipment utilizing a conventional agricultural subsoiler consisting of a vertical blade on which a chisel, or foot, was mounted at an angle of approximately 15° from horizontal. A piece of metal tubing was attached to the blade which terminated 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 pesticide immediately behind the chisel. The equipment, with two injectors, was calibrated and application at 250 lbs/acre equivalent of 2,4-D was made on one-foot and on two-foot centers in the two plots.

During the process of application the overlying vegetative structure of greasewood was to all intents and purposes destroyed. The soil structure itself, to a depth of approximately 12", was drastically altered; particularly on the plot having one-foot centers. Roughness of terrain tended to cause considerable variation in the depths at which the waste chemical was injected, and in a few instances, material appeared on the surface.

Data derived from samples taken from these plots are summarized in Figures 14 and 15. Because of the extent by which the soil was broken up, waste distribution and sample variation was very large and the analytical data exhibit considerable scatter. There is, however, strong evidence of a decline in concentrations within the 480 day period under report for both the plots.

These applications were made in the late summer, and during the fall and winter the odor of phenolic volatiles was not readily detected. It was apparent, however, the following year that during the high temperature extremes, that the broken soil structure was permitting escape of some of the volatile phenolic components. Removal of the vegetative structure during the process of application created concern as to possibility of wind erosion. However, during the

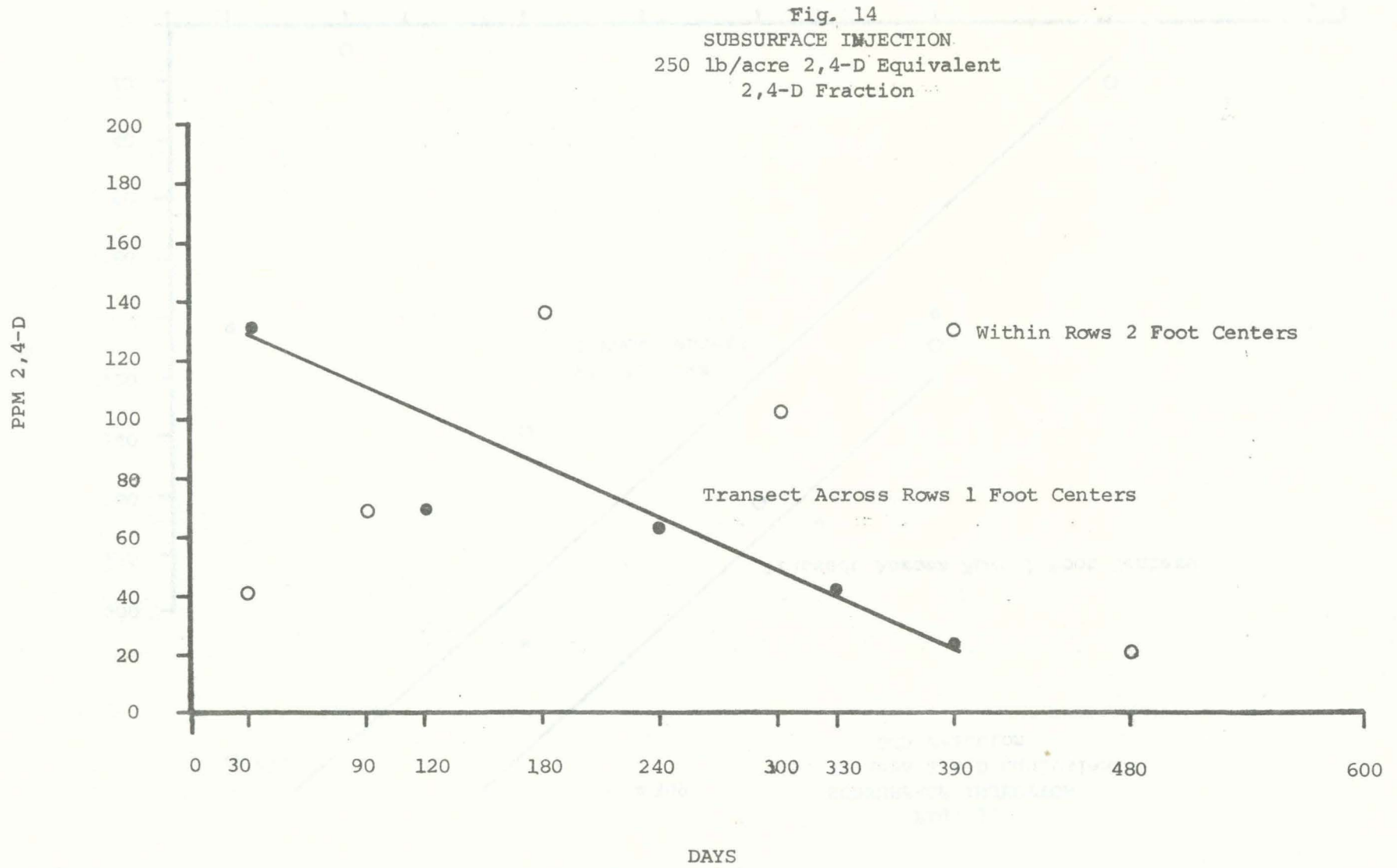
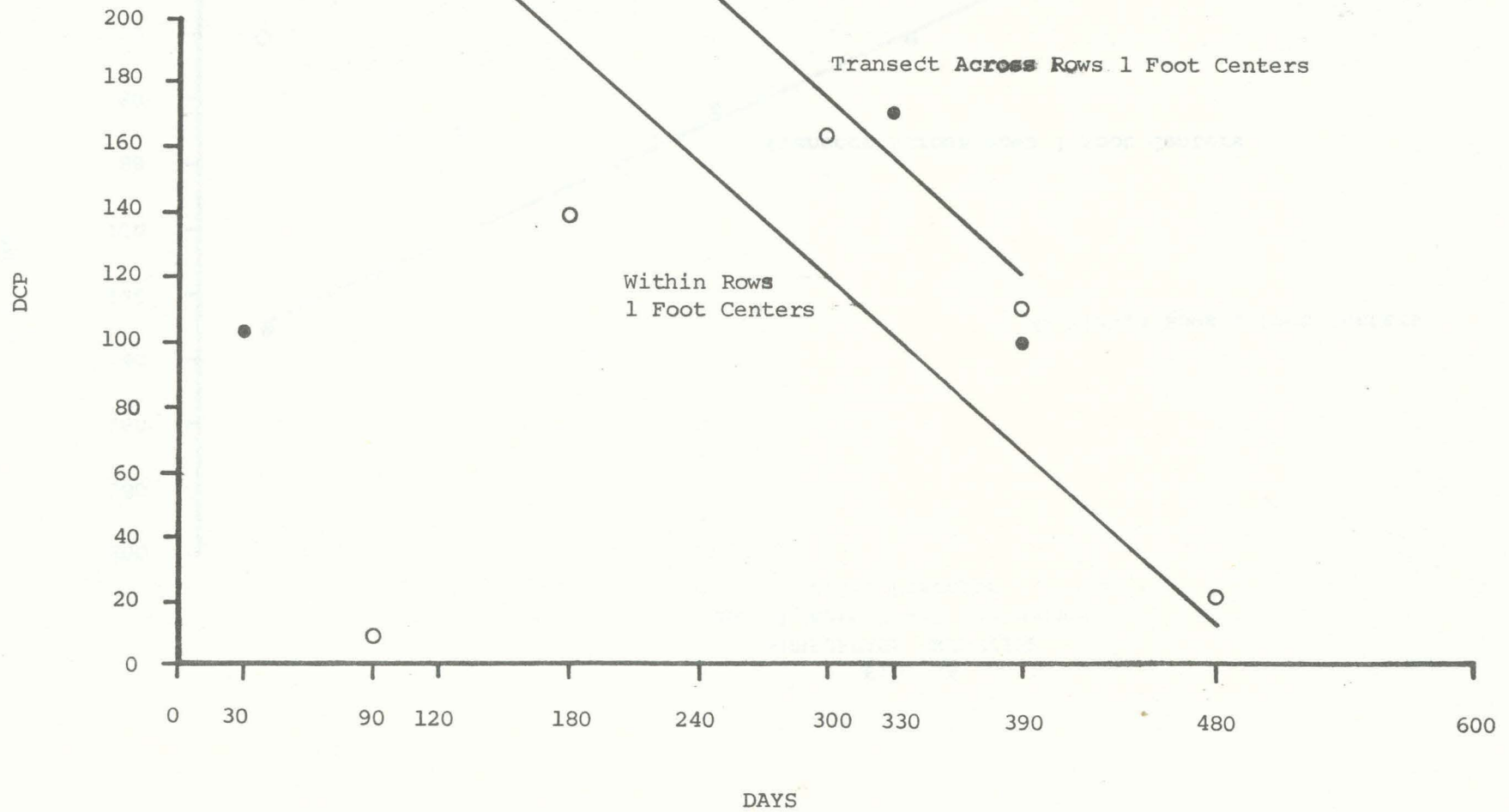


Fig. 15
SUBSURFACE INJECTION
250 lb/acre 2,4-D Equivalent
DCP Fraction



summer and fall following treatment, effects of erosion were not observed in any appreciable degree. Broken remnants of the greasewood shrubs which remained imbedded at the soil surface may have contributed to this. Observations continue on these subsurface injection plots as well as other, more extensive treatments which have been conducted during the fall of 1971.

HERBICIDAL EFFECTS

Early in the development of this program, it was determined that both sagebrush and greasewood were susceptible to the waste material used as an herbicide. Subsequent to these observations, and very late in the growing season of 1970, a total of 16 acres of typical greasewood-sagebrush vegetation was treated at rates of 4, 8 and 16 lbs 2,4-D equivalent per acre. Normal applications of 2,4-D alone, for this purpose in eastern Oregon, range from approximately 2 lbs to 6 lbs/acre. Results of these applications, when they became completely evident the following spring, indicate a very high level of control of the greasewood at all rates of application and a useful level of control of the sagebrush species present. More importantly, the native grasses present survived without apparent effect. Reduction in competition from the undesirable rangeland shrubs characteristically results in stimulation in growth of bunch grass and other desirable range grasses. During the spring of 1972, these plots, as well as approximately 10 acres of land subject to subsurface injections, will be seeded with test varieties of range grasses to estimate the effects of these treatments upon productivity.

Management of Spent Pesticide Containers

FIG. 16. The Problem: Uncontrolled dump sites used for spent pesticide containers.



Pesticidal chemicals will continue to be widely used and accepted as an integral part of this nation's food and fibre production complex. It has been estimated that, nationally, about a billion pounds of pesticidally-active ingredients were sold in 1970, resulting in the use of about 130 million containers. Because of the construction of the openings in most containers for liquids, significant quantities of concentrate are left behind in the containers after use. Field rinsing with the formulated pesticide and addition of the rinse to the spray tank will materially reduce this residue. Unfortunately, even the residue from field rinsing may be too large for conventional means of container disposal.

These containers, varying in size from 1-pint to 55-gallon capacities are now buried, crushed or discarded in a variety of hazardous and unsatisfactory ways (Fig. 16). This practice constitutes a multiple loss; for not only is the steel or other material in the container (weighing up to 35 pounds) lost to reuse, but the once useful contents are free to leach into and contaminate the soil and groundwater at innumerable unsupervised disposal sites.

About two years ago, through the action of the Agricultural Chemicals Committee of Klamath County, a cooperative effort to collect and manage these containers was initiated involving Klamath County and Oregon State University's Environmental Health Science Center, and the Pesticide Management Facility at Merrill, Oregon was brought into existence.

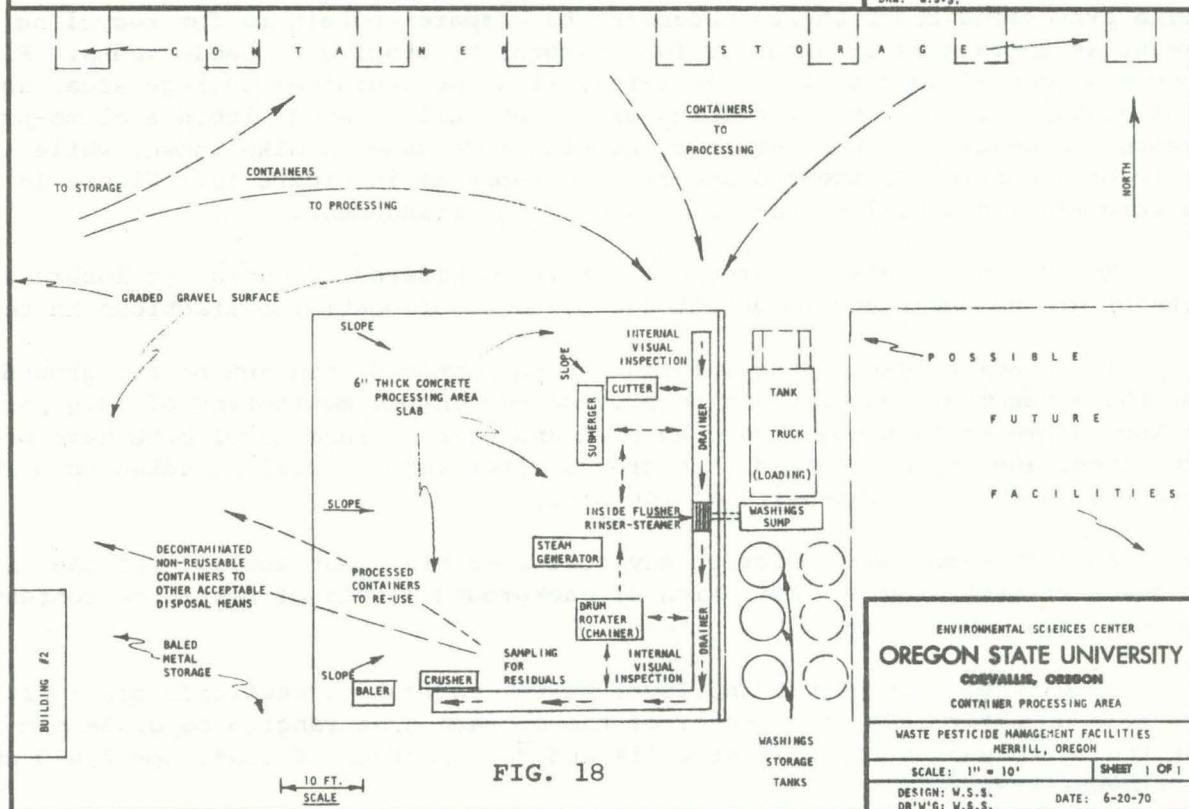
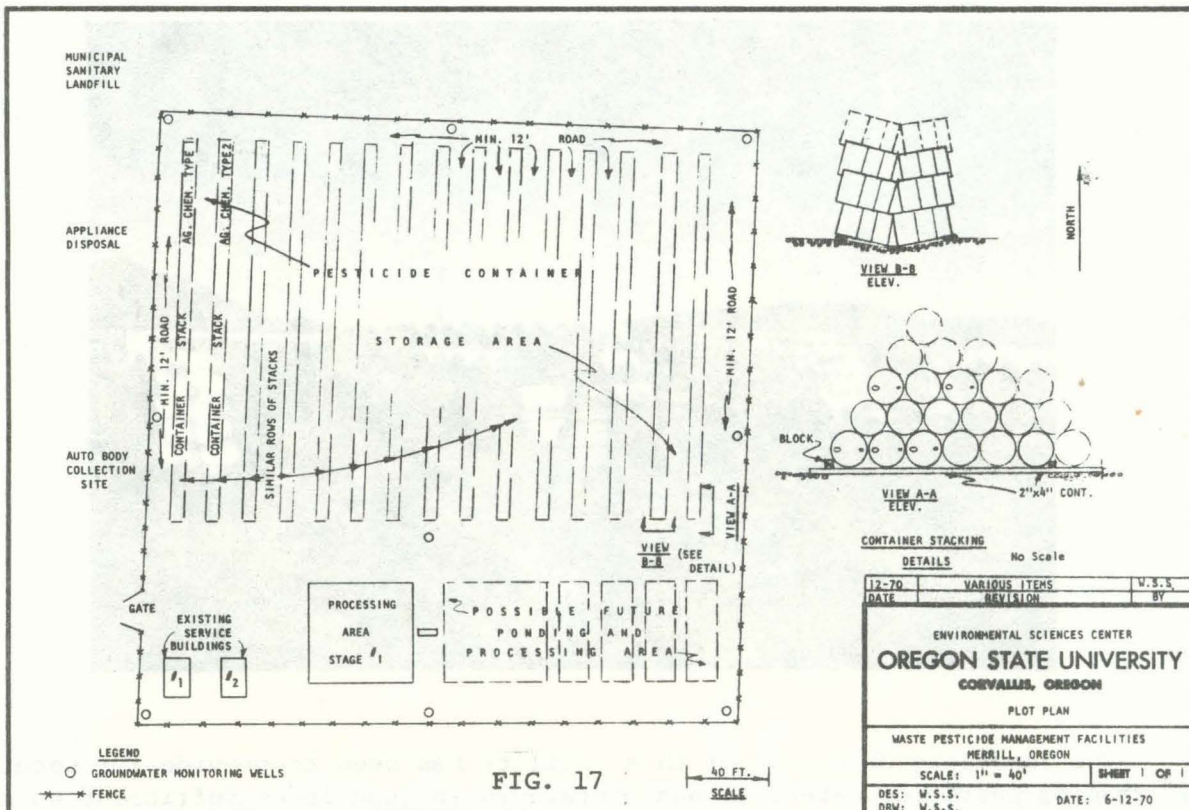


FIG. 19. Portion of Storage Area, Merrill, Oregon Container Site.



The immediate objective of this facility has been to provide for secure storage of pesticide materials and containers in quantities sufficient to determine processing requirements necessary to prepare containers for recycling for reuse as containers or scrap or for disposal by other acceptable means. Figure 17 shows a general layout of the facility, with the container storage area, service buildings, and concrete processing area slab, all located within a climb-proof fence. A detail of the container stacking mode used is also shown, while a picture of a portion of the storage area is shown as in Figure 19. Figure 18 shows a larger-scale detail of the processing area arrangement.

Monitoring of air and ground water is considered essential to insure security of ground water and to detect the presence of pesticide fractions in the air.

To establish background information on pesticide content of the ground water at the Management Facility and to provide continuous monitoring of this parameter, 3-inch diameter test holes were augered and cased. Base level data have been obtained, and it is intended that ground water samples will be taken on a regular basis as a check on integrity of the site.

Samples were taken prior to any container treatment activity at the site as a means of providing an indication of background levels of pesticide content in the ground water under the site.

Results of this background level survey indicate a pesticide concentration of zero directly under the center of the storage area ranging to 0.038 ppm 2,4-D at the south and southwest test wells and to a maximum of 0.053 ppm 2,4-D at the northwest test well.

It may be significant that the highest indicated concentration occurred immediately adjacent to the Klamath County dump where solid waste has been buried for a number of years. However, these concentrations are so very small that the reliability of the results as indicators of 2,4-D content of the ground water, from whatever source, is questioned since it is possible that such minute concentrations could result from sampling equipment contamination from other work in progress.

Air sampling has been initiated by mounting a 24" X 24" X 1" glasswool filter on the fence on each of the four sides of the site and one control collector approximately 1/2 mile from the site. Removal and laboratory testing of the filter materials for volatiles and other pesticide fractions will be done on a regular basis.

Some alternatives considered for the operation of a pesticide container management facility such as the one at Merrill were:

1. Complete processing at each management facility.
2. Preprocessing to a safe level at the facility with subsequent movement of the containers to a central, perhaps regional, facility for further processing to a level necessary for reuse or safe disposal through more conventional channels.
3. A mobile container-processing unit, moving from management facility to management facility with specialized equipment mounted on a trailer or trailers, which would have the capability of cleaning containers to residual levels necessary for reuse, reprocessing or safe disposal.

Because of the large investment necessary for commercial-type container reconditioning and cleaning equipment and the intermittent nature of the operation contemplated at typical management facilities of this type, it was decided in this preliminary stage of operation, to hold major equipment purchases to a minimum, acquiring or building needed equipment as determined by initial operations.

The general categories of operations contemplated at the facility are:

Mechanical - Including abrading of residuals from interior surfaces by means of drum rotators in combination with chains introduced through the bung holes.

Chemical - Including submergence in solutions at ambient or elevated temperature, stripping of residual contents by caustic and other chemical solutions, and other means.

Mechanical-Chemical Combinations - Including hot steam-chemical solutions introduced by jet action into the interior, agitation while submerged, and other possible combinations of the preceding categories.

In order to design a process line which would be capable of performing all of the functions necessary to render containers reuseable as containers or scrap, or at least permit their release from the management facility as non-hazardous solid waste, a survey was made of various barrel and drum reconditioning equipment, and several commercial reconditioning facilities were visited.

Unit processes utilized by the barrel and drum reconditioning industry have been modified and incorporated into a pilot process line which will be used to clean containers to acceptable residual levels. Reduction of residuals in containers to acceptable levels have been initially attempted without opening the containers. Cleaning operations by mechanical and chemical means are performed through the existing bungs in the same manner that the container reconditioning industry performs these operations. Processed containers are so sampled so that the cleaning effectiveness of various combinations of agents may be accurately evaluated.

Current pilot process line sequences include combinations of the following unit operations:

1. Submerge - Place containers in submerger containing water or solutions at ambient or elevated temperatures for varying lengths of time required to clean with varying types and concentrations of solutions.
2. Chainer - Introduce chains through bung hole and rotate containers on chainer device for physical abrading and removal of internal deposits.
3. Internal Flush, Rinse, Steam - Subject interior surfaces to high pressure flushing with various combinations of water, steam, and solutions at both ambient and elevated temperatures.
4. Internal Spray Rinse - Place container bung hole over single high pressure nozzle and impinge spray on all surfaces.
5. Internal Visual Inspection - Determine amount of contents and condition of internal container surfaces, using quantitative as well as qualitative evaluation techniques both before and after processing.
6. Drain - Empty existing contents or that remaining after submergence.
7. Open Containers - Expose interior surfaces for careful evaluation of condition both before and after processing.
8. Sampling for Residuals - This operation will include sampling of surfaces for exhaustive laboratory examination as an evaluation of process effectiveness.

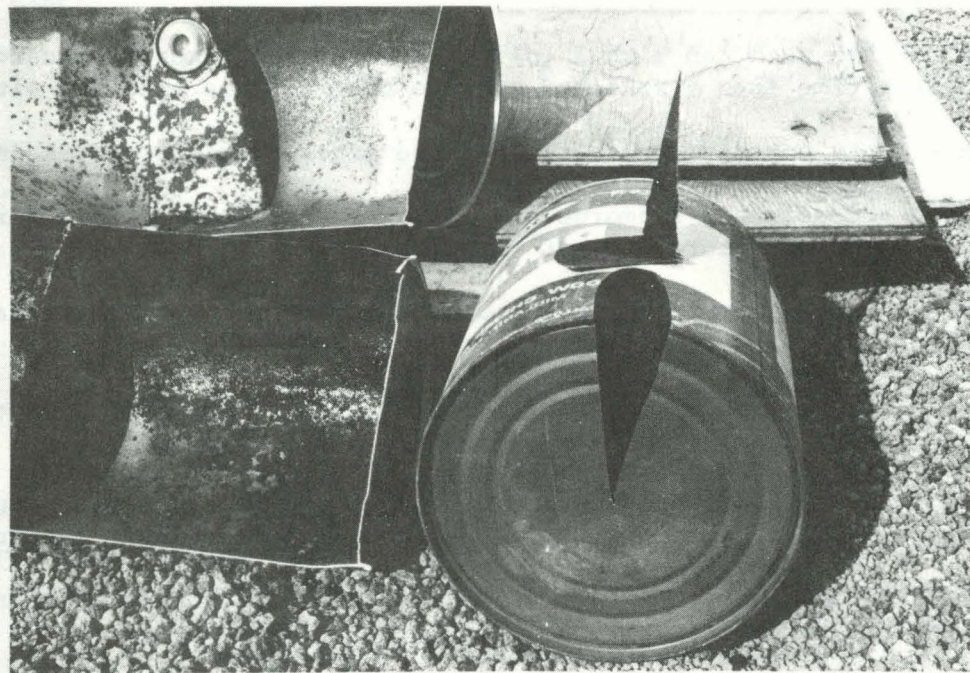
Location of these unit operations in relation to one another are shown in Figure 18.

Off-site completion of "open-ended" processes:

9. Transport to further processing or reuse as containers.
10. Recycle as scrap.
11. Incorporate into sanitary landfill.

The sequences of unit operations are developed to allow tests for the most effective combinations of actions for each type of container and group of pesticides.

FIG. 20. Opened container showing rust and aged residues. Metal sample segment used for analysis appears on right.



A series of pilot tests designed to evaluate relative cleaning effectiveness of cleaning solutions have been completed on a number of standard-sized representative pieces cut from tops and bottoms of containers "spiked" in a uniform manner (Fig. 20). A commercial formulation of 2,4-D ester was chosen as a representative class of chemical and metal samples were taken from "spiked", aged 2,4-D containers. Solutions of: 5% heavy duty detergent; 5% tri-sodium phosphate; 1% caustic soda, and; Oakite industrial rust remover were applied to metal samples at an ambient temperature of about 20°C. and at 82°C.

Preliminary analytical data from extracts of the 2,4-D container metal indicate pesticide residuals in samples treated at ambient temperature to be three to ten times as high as those treated at the elevated temperature.

The cleaning effectiveness of the various solutions was not found to vary greatly from one solution to another, even at elevated temperature, except that the residual in samples treated with detergent was about two to three times that remaining after treatment with the other three solutions. More studies on relative effectiveness of cleaning solutions are planned in whole cans rather than in metal segments.

A second series of pilot tests was run on "spiked" 2,4-D containers to analyze only the relative cleaning effectiveness of individual unit operations.

These operations, whose sequence and effects are summarized in Table 3, are described as follows:

1. Raw Can - An aged 2,4-D ester spent 5-gallon container.

2. Spike - Add 1/2 gallon agricultural chemical to can. Rotate to cover all interior surfaces then pour back into measurer, draining as completely as possible. Record amount remaining in can. Make up material in measurer to 1/2 gallon and repeat on next can until all have been treated.
3. Rinse - Rinse each can with 1 gallon of water two times. Discard rinse water each time into a selected storage drum. Rinse exterior with hose.
4. Drain - Empty contents or that remaining after previous processing.
5. Submerge - Completely submerge all surfaces of can in plain water at ambient air temperature. Time: 1 hour.
6. Steam - Inject steam into can through bung hole attempting to reach all surfaces. Time: 1 minute.
7. Chainer - Rotate can on chainer with 5 ft. length of chain for 5-gallon drums. Time: 10 minutes each axis.
8. Jet-Rinse - Place can bung hole over single nozzle and impinge spray on all interior surfaces at about 100 psi and 25 gpm. Time: 1 minute.
9. Sample - Expose and inspect interior surfaces. Cut three standard wedges from top and three from bottom of can.

Results indicate the greatest reduction in residual pesticides occurred during the Sequence H, which included all unit operations. However, this reduction was not sufficiently greater than those achieved through jet-rinsing or steam and jet-rinsing spiked cans. This may warrant the conclusion that the full combination of all units was really no more effective than some of the shorter sequences. Some deductions may be made as to the relative effectiveness of the individual units; however, additional studies must be conducted before full evaluation can be made. Preliminary observations involving only two sets of samples from two cans reported under Sequence C, indicate a very high order of effectiveness associated with one hour of submergence and drainage. Sequence D indicates steam to be effective in a similar order of magnitude. The effects of chaining need additional studies since this unit operation needs to be combined with a rinse or a submergence, followed by draining in order to completely assess its relative effectiveness. Under the conditions of Sequence F, the jet rinse alone, appears about as effective as Sequence H, which includes all unit operations. Steam plus the jet rinse, illustrated in Sequence G, shows a higher average than either F or H. However, in all probability, all three of these sequences produced somewhat similar results when the relatively small numbers of samples and the amount of variation in analytical data between can samples are considered. The rather large variations appearing in Sequences A through E, may be the result of sample metal being taken from a portion of the can where aged residues had accumulated in storage.

Extrapolation from the mean pesticide residuals in Sequences G and H, indicate a reduction to 1-2 gms of pesticide per 5-gallon container, using steam or jet rinse, or a combination of all units, but without any specific chemicals or cleaning agents.

Table 3.

Summary: Cleaning Effect of Unit Operations in Experimental Sequences.

Unit Operation	Sequence of Unit Operations Performed							
	A	B	C	D	E	F	G	H
Raw can	X	X	X	X	X	X	X	X
Drain	X	X	X	X	X	X	X	X
Spike		X	X	X	X	X	X	X
Rinse		X	X	X	X	X	X	X
Drain		X	X	X	X	X	X	X
Submerge			X					X
Drain			X					X
Steam				X			X	X
Chain					X			X
Jet Rinse						X	X	X
Drain				X	X	X	X	X
Sample	X	X	X	X	X	X	X	X
	A	B	C	D	E	F	G	H
mg 2,4-D	722	737	129	142	134	31	132	29
Residual	207	393	55	308	454	75	32	34
Per can	145	863		95	186	47	134	45
Sample	178			28	331	20	8	26
	472			37	76	59	53	49
	246							63
	307							
	325							
\bar{X}	325	664	92	122	236	48	72	41

Separate collection and storage of washwaters generated by each operation will be on the basis of compatibility of pesticide characteristics and ultimate disposal requirements. Adequate valving is available to enable pumping from the washwater collection sump to tank trucks, to tank storage or to lagoon storage, depending upon quantity of liquid and disposal requirements. It is possible that practical uses will be found for some washwaters through addition of pesticide for recommended uses such as fly control at landfill sites and control of vegetation in non-critical areas.

A pesticide management site located adjacent to other waste management facilities, such as that at Merrill, might be expected to take advantage of this proximity. The Merrill scrap auto body collection site receives approximately 600 car bodies during an average year of operation. Stripped of motors, wheels, glass, upholstery, wood and plastics, the weight of steel might be expected to average approximately 2500 pounds per auto body. Study has shown that steel containers, not reuseable as containers and cleaned to a level shown possible in pilot studies at Merrill, could be combined with these car bodies as a means

of providing a "dilution factor" for the residual pesticide in the scrap mixture. The resulting scrap mixture, using a ratio of twenty five-gallon containers, or it's equivalent, per car body, would have a residual pesticide concentration of about 55 parts per million or 0.11 pounds per ton of scrap. At this rate of combination, it is estimated that the scrap auto collection facility at Merrill could absorb 12,000 five-gallon containers annually, which is more than the expected annual container use rate for the county.

The scrap-to-steel ratio at point of reuse would further reduce the pesticide concentration such that stack emissions of pesticide residuals would be a small part of the scrap contaminants scrubbed out with other stack materials. Study of this aspect of the potential reuse stream will continue.