



Decomposition rates of residual crude oil in soil : a comparison of soil amendments
by Michael Francis Cormier

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Land Rehabilitation

Montana State University

© Copyright by Michael Francis Cormier (1989)

Abstract:

Terrestrial spills of refined and crude oil adversely effect the productive capability of contaminated lands by inhibiting or eliminating vegetative growth. One practical approach to the correction of the problem posed by oil spills is to improve the conditions under which natural biodegradation of the spilled material takes place.

Ten different treatments were applied to soil contaminated with weathered crude oil at a site in north-central Montana using a combination of amendments including tillage, fertilization, irrigation, mulch, plastic sheeting, inoculum, and calcium chloride. Treatments were evaluated over a 10 1/2 month period. Pretreatment soil oil content in the 0 to 5 cm depth interval was 5.20 percent by weight, decreasing with depth to 1.40 and 0.41 percent oil by weight in the 5 to 15 and 15 to 46 cm intervals, respectively.

Tillage and chiseling were basic amendments applied to all treatments except the control. A significant reduction in soil oil content was noted (65%) in the 0 to 5 cm interval one day after their application, a result of the mixing of soil to a depth of 15 to 20 cm.

Following tillage, none of the treatments had significantly ($P=0.05$) higher degradation rates than the control over the term of the study. The combination of tillage, fertilizer, and calcium chloride exhibited the greatest decrease in soil oil content (22%), however.

This treatment also had significantly higher infiltration than non-contaminated soil as well as all other treatments. The increase in infiltration was attributed to flocculation of the dispersed sodic soils. Tilled plots also had significantly higher infiltration than non-tilled plots, suggesting that aeration and water flux is an important factor in oil degradation. Plots covered with plastic sheeting significantly increased soil temperatures above temperatures measured on non-covered plots at all depths but this increase did not influence the rate of degradation on plots covered with sheeting.

None of the other amendments were found to improve oil degradation. Two factors were primarily responsible for this result. The distribution of oil on the site was extremely variable, limiting the precision of the experimental design. In addition, soils were monitored for a relatively short period of time. In the cold, dry environment of the Northern Great Plains, even enhanced degradation of oil probably occurs at a slow rate.

DECOMPOSITION RATES OF RESIDUAL CRUDE OIL IN SOIL:

A COMPARISON OF SOIL AMENDMENTS

by

Michael Francis Cormier

A thesis submitted in partial fulfillment
of the requirements for the degree

of

Master of Science

in

Land Rehabilitation

MONTANA STATE UNIVERSITY
Bozeman, Montana

January 1989

N378
@ 8135
cop. 2

APPROVAL

of a thesis submitted by

Michael Francis Cormier

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

January 6, 1989
Date

D. J. Dollhoff
Chairperson, Graduate Committee

Approval for the Major Department

1-6-89
Date

Arthur E. Winter
Head, Major Department

Approval for the College of Graduate Studies

January 17, 1989
Date

Henry S. Parsons
Graduate Dean

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a master's degree at Montana State University, I agree that the Library shall make it available to borrowers under rules of the Library. Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledgment of source is made.

Permission for extensive quotation from or reproduction of this thesis may be granted by my major professor, or in his absence, by the Dean of Libraries when, in the opinion of either, the proposed use of the material is for scholarly purposes. Any copying or use of the material in this thesis for financial gain shall not be allowed without my written permission.

Signature Michael Conner

Date January 6, 1989

ACKNOWLEDGMENTS

I would like to thank the members of my graduate committee, Dr. Douglas J. Dollhopf, Dr. Frank Munshower, and Dr. William Inskeep for their helpful advice and willingness to lend me equipment and technical support. I would also like to thank the members of Montana Salinity Control Association Jane Holzer, Mark Tomer, Glen Hockett, Tim Kuehn, and Scott Brown for their assistance in the field and advice and good humor. I am also indebted to Martha Gitt whose numerous suggestions and editing improved the content of the final draft. Special thanks go to MSI Detoxification, Inc., Kevin Harvey, and Bob Crayton whose much appreciated involvement kept me in the black along the way.

TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS	iv
TABLE OF CONTENTS	v
LIST OF TABLES	vii
LIST OF FIGURES	x
ABSTRACT	xi
INTRODUCTION	1
LITERATURE REVIEW	3
Composition of Crude Oil	3
Effect of Oil on Soil	4
Effect of Oil on Plant Growth, Germination, and Production	6
Degradation of Crude Oil	9
Pathways of Degradation	9
Increasing the Rate of Biodegradation Using Soil Amendments	11
Tillage	11
Fertilization	12
Irrigation	14
Temperature modification	14
Liming	15
MATERIALS AND METHODS	16
Site Description	16
Preliminary Soil Sampling	19
Experimental Design and Treatment Installation	21
Field Measurements	25
Infiltration	25
Temperature Monitoring	25
Analytical Methods	26
Soil Sample Preparation	26
Oil Extraction	26
Fertility	27
Statistical Analysis	28

TABLE OF CONTENTS -- continued

	Page
RESULTS AND DISCUSSION	30
Experimental Error	30
Soil Oil Content	32
Soil Oil Content in the 0 to 5 cm Depth Interval	32
Soil Oil Content in the 5 to 15 cm Depth Interval.	36
Soil Oil Content in the 15 to 46 cm depth interval	38
Comparison Contrasts of Soil Amendments.	41
Fertility	42
Infiltration	43
Temperature	45
SUMMARY AND CONCLUSIONS	47
LITERATURE CITED	50
APPENDIX: Analysis of Variance Tables.	56

LIST OF TABLES

Table	Page
1. Chemical composition of Madison oil.	19
2. Soil characteristics of the Shay-Wait site.	20
3. Treatments applied to Shay-Wait plots.	23
4. Summary statistics of soil oil in the 0 to 5 cm depth interval	32
5. Changes in soil oil content in the 0 to 5 cm depth interval.	33
6. Summary statistics of soil oil in the 5 to 15 cm depth interval	36
7. Changes in soil oil content in the 5 to 15 cm depth interval	37
8. Summary statistics of soil oil in the 15 to 46 cm depth interval	39
9. Changes in soil oil content in the 15 to 46 cm interval. . .	39
10. Average soil nitrate-nitrogen before and after fertilization.	42
11. Soil temperature on plastic covered and non-covered plots . .	46
12. Analysis of variance and treatment means for pretreatment soil oil content in the 0 to 5 cm depth interval.	57
13. Analysis of variance and treatment means for the difference in soil oil content between tilled treatments and the control in the 0 to 5 cm depth interval	57
14. Analysis of variance, treatment means, and least significant difference sets for the difference in soil oil content between the 205 and one day soil samples in the 0 to 5 cm depth interval.	58
15. Analysis of variance, treatment means, and contrast coefficients for the difference in soil oil content between the 315 and one day soil samples in the 0 to 5 cm depth interval.	59

LIST OF TABLES -- continued

Table	Page
16. Analysis of variance and treatment means for pretreatment soil oil content in the 5 to 15 cm depth interval	60
17. Analysis of variance and treatment means for the difference in soil oil content between tilled treatments and the control in the 5 to 15 cm depth interval.	60
18. Analysis of variance and treatment means for the difference in soil oil content between the 205 and one day soil samples in the 5 to 15 cm depth interval.	61
19. Analysis of variance, treatment means, and contrast coefficients for the difference in soil oil content between the 315 and one day soil samples in the 5 to 15 cm depth interval.	62
20. Analysis of variance and treatment means for pretreatment soil oil content in the 15 to 46 cm depth interval.	63
21. Analysis of variance and treatment means for the difference in soil oil content between tilled treatments and the control in the 15 to 46 cm depth interval	63
22. Analysis of variance and treatment means for the difference in soil oil content between the 205 and one day soil samples in the 15 to 46 cm depth interval	64
23. Analysis of variance, treatment means, and contrast coefficients for the difference in soil oil content between the 315 and one day soil samples in the 15 to 46 cm depth interval.	65
24. Analysis of variance and treatment means for pretreatment nitrate-nitrogen content in the 0 to 5 cm depth interval. . .	66
25. Analysis of variance, treatment means, and contrast coefficients of nitrate-nitrogen content in the 0 to 5 cm depth interval in the 315 day samples	66
26. Analysis of variance and treatment means for pretreatment phosphorus content in the 0 to 5 cm depth interval.	67
27. Analysis of variance and treatment means for pretreatment potassium content in the 0 to 5 cm depth interval	67

LIST OF TABLES -- continued

Table	Page
28. Analysis of variance and treatment means for pretreatment nitrate-nitrogen content in the 5 to 15 cm depth interval . . .	68
29. Analysis of variance, treatment means, and contrast coefficients for nitrate-nitrogen content in the 5 to 15 cm depth interval in the 315 day samples	68
30. Analysis of variance and treatment means for pretreatment phosphorus content in the 5 to 15 cm depth interval	69
31. Analysis of variance and treatment means for pretreatment potassium content in the 5 to 15 cm depth interval.	69
32. Analysis of variance and treatment means for pretreatment nitrate-nitrogen content in the 15 to 46 cm depth interval. .	70
33. Analysis of variance, treatment means, and contrast coefficients for nitrate-nitrogen content in the 15 to 46 cm depth interval in the 315 day samples	70
34. Analysis of variance and treatment means for pretreatment phosphorus content in the 15 to 46 cm depth interval.	71
35. Analysis of variance and treatment means for pretreatment potassium content in the 15 to 46 cm depth interval	71
36. Analysis of variance, treatment means, least significant difference sets, and contrast coefficients for infiltration data.	72

LIST OF FIGURES

Figure	Page
1. Location of Shay-Wait study site.	16
2. Average monthly temperature and precipitation.	17
3. Plan view of experimental design.	22
4. Coefficients of variation calculated from extracted oil values measured in soil samples collected 205 days after treatment.	31
5. Average soil oil content in the 0 to 5 cm depth interval . .	33
6. Average soil oil content in the 5 to 15 cm depth interval. .	37
7. Average soil oil content in the 15 to 46 cm depth interval .	40
8. Infiltration rates of selected treatments.	43
9. Infiltration rates of selected treatments	44

ABSTRACT

Terrestrial spills of refined and crude oil adversely effect the productive capability of contaminated lands by inhibiting or eliminating vegetative growth. One practical approach to the correction of the problem posed by oil spills is to improve the conditions under which natural biodegradation of the spilled material takes place.

Ten different treatments were applied to soil contaminated with weathered crude oil at a site in north-central Montana using a combination of amendments including tillage, fertilization, irrigation, mulch, plastic sheeting, inoculum, and calcium chloride. Treatments were evaluated over a 10½ month period. Pretreatment soil oil content in the 0 to 5 cm depth interval was 5.20 percent by weight, decreasing with depth to 1.40 and 0.41 percent oil by weight in the 5 to 15 and 15 to 46 cm intervals, respectively.

Tillage and chiseling were basic amendments applied to all treatments except the control. A significant reduction in soil oil content was noted (65%) in the 0 to 5 cm interval one day after their application, a result of the mixing of soil to a depth of 15 to 20 cm.

Following tillage, none of the treatments had significantly ($P=0.05$) higher degradation rates than the control over the term of the study. The combination of tillage, fertilizer, and calcium chloride exhibited the greatest decrease in soil oil content (22%), however. This treatment also had significantly higher infiltration than non-contaminated soil as well as all other treatments. The increase in infiltration was attributed to flocculation of the dispersed sodic soils. Tilled plots also had significantly higher infiltration than non-tilled plots, suggesting that aeration and water flux is an important factor in oil degradation. Plots covered with plastic sheeting significantly increased soil temperatures above temperatures measured on non-covered plots at all depths but this increase did not influence the rate of degradation on plots covered with sheeting.

None of the other amendments were found to improve oil degradation. Two factors were primarily responsible for this result. The distribution of oil on the site was extremely variable, limiting the precision of the experimental design. In addition, soils were monitored for a relatively short period of time. In the cold, dry environment of the Northern Great Plains, even enhanced degradation of oil probably occurs at a slow rate.

INTRODUCTION

Terrestrial spills of refined and crude oil adversely effect the productive capability of contaminated lands by inhibiting or eliminating vegetative growth. Rowell (1977) estimated that an average of 69,000 barrels of oil was spilled each year in Alberta, Canada. In Montana, 150 incidents of petroleum spills were reported in 1987 (John Arrigo, personal communication, Montana State Department of Health and Environmental Sciences, Water Quality Bureau).

The effects of a spill may last for decades if left to natural processes (McGill 1977). In Montana, there are many oil and gas fields which harbor contaminated soils. Oil leaks and spills were common occurrences in the early years of oil exploration, a result of everyday production operations. Cleanup of these spills is difficult because a large proportion of them are small in size and are located in remote areas. In addition, responsible parties cannot often be identified due to changes in leasehold or land ownership. Removal of spilled oil, then, is left in the hands of the current landowner who has few resources to commit to the cleanup of contaminated land.

Although many researchers have investigated the degradation of crude oil in soils, no field studies have been conducted on highly weathered residual oils. The purpose of this study was to determine if degradation of residual crude oil could be enhanced with the use of

soil amendments under the environmental conditions encountered in the Northern Great Plains. The objectives of this study were:

1. Test soil amendments which could be implemented by local landowners encumbered with oil contaminated soils.
2. Monitor the rate of decomposition of oil by measuring soil oil content at selected intervals.
3. Monitor soil physical and chemical parameters through time, including infiltration, soil temperature, and soil fertility.

LITERATURE REVIEW

Composition of Crude Oil

Petroleum hydrocarbons in crude oil can be broken down into three general classes: the saturate or aliphatic fraction, aromatics, and asphaltics (Atlas 1981). The saturate fraction includes alkanes (normal and iso), branched alkanes, and cycloalkanes. As a group, the saturate fraction accounts for the largest percentage of all compounds found in crude oil and are commonly referred to as waxes or paraffins. Alkanes with carbon numbers of up to C₇₈ are known to occur, although most have carbon numbers from C₁ to C₃₃ (Rowell 1977). The cycloalkanes (naphthenes) are saturated cyclic compounds isolated in the C₄ to C₁₁ carbon range. Aromatic hydrocarbons contain a benzene ring and are found in both the low and high boiling range. The asphaltic fraction is composed of tar-like heavy fractions of crude, collectively known as resins. This fraction includes very complex ring structures, mixed condensed aromatic and cyclic ring compounds, and nonhydrocarbon polar components composed of nitrogen, sulfur, and oxygen (Bartha 1986).

Metals are also present in some crude oils, particularly vanadium- (Baker 1970). Other metals including manganese, nickel, lead, selenium, mercury, zinc, chromium, and cobalt may also be present (Rowell 1977).

Effect of Oil on Soil

As oil is added to a soil it percolates downward through the profile, displacing air and water and adsorbing onto soil particles and organic matter. Heavy oil fractions are filtered out at the surface while lighter components pass to greater depths (Plice 1948). This wetting of the soil with oil brings about significant physical and chemical changes, most notably in soil redox potential, pH, temperature, wettability, and nitrogen and organic carbon content.

The redox potential of the soil changes from an aerobic condition to an anaerobic one if the oil content reaches high enough levels (Plice 1948; Schwendinger 1968; Rowell 1977). Oil increases the oxygen demand of a soil as it is oxidized during the degradation process (Dotson et al. 1970; Bartha 1986). Ellis and Adams (1961) reported a redox reduction from +0.833 mV to -0.982 mV in one soil following the addition of oil.

Changes in soil pH are dependent on the buffering capacity of the soil and the pH of the contaminating crude. Skujins and McDonald (1985) reported a pH of 2.7 for waste industrial oil. Dibble and Bartha (1979b) reported an increase of 0.3 pH units from 6.2 for an uncontaminated soil to 6.5 for soil contaminated with kerosene.

Soil temperature is primarily affected by the change in color of the soil surface. Most crude oils are brown, black, or green. These dark colors increase the absorption of radiant energy when spilled on a lighter colored soil. An increase of 5 to 9.5°C has been noted between oiled cultivated plots and unoiled, cropped plots at a depth of 15 cm (Toogood 1977).

Reduction in the wettability of the soil has been noted. Oil contamination over 0.5% by volume has been shown to reduce water uptake (de Jong 1980b). Severely contaminated sites exhibited considerably reduced soil-water uptake. Oil coated particles of soil resist the absorption of water, in one case reducing water uptake of a loamy soil by 50 to 75% during the first 5 minutes of wetting (Toogood 1977). After exposure to the atmosphere and sun, oil on the surface gradually thickens, eventually turning into a hard crust (Plice 1948; Mitchell, Loynachan, and McKendrick 1979). Once a surface crust develops, it becomes an effective barrier to water infiltration. Oiling of the soil also causes a breakdown of structure and dispersion of soil aggregates (Plice 1948). This may be due to the solvent properties of the lighter portions of the oil, which dissolve gums and waxes cementing aggregates together (Rowell 1977). Loss of structure and dispersion further affect soil-water relationships.

The carbon to nitrogen ratio (C:N) in an oiled soil rises dramatically due to the carbon contribution of the oil. Plice (1948) reported an organic matter content of 11.45% (\approx 6.7% organic carbon) and a total nitrogen level of 0.12% for a soil containing 6.77% oil. This translates to a C:N ratio of 56:1. Optimum C:N ratios for biological activity are in the 10:1 range (Donahue et al. 1983). Crude oils do contain 0.01% to 0.9% nitrogen (Toogood 1977; Brown et al. 1981) but this nitrogen is not necessarily available for use by organisms. Nitrogen does become available after degradation of the oil has been initiated.

Effect of Oil on Plant Growth, Germination, and Production

In the initial period following contamination, oil contacting vegetation adversely affects fine roots and root hairs (Bartha 1986). This inhibits water and nutrient uptake, killing some plants and suppressing the growth of others (Carr 1919; de Jong 1980b). Plants are able to take up some oil components from contaminated soil. In general, the smaller the hydrocarbon molecule, the more toxic the oil is to plants (Baker 1970). Volatile hydrocarbons have been shown to be extremely potent (Currier 1951 reported by Rowell 1977). Hydrocarbons within the 150 to 275°C boiling range (naphtha and kerosene) are also considered toxic and remain in the soil far longer than volatile fractions. Heavier oil fractions, however, have molecules that may be too large to penetrate plant tissues (Baker 1970), leaving them potentially less troublesome to plant growth.

Revegetation of an area contaminated with oil is governed by the adverse changes to the soil mentioned previously and direct effects of oil on plant growth and germination. These effects include the loss of a viable seed source, the creation of a poor seedbed, and an increase in competition for nutrients. Seed that was in the ground at the time of contamination is highly susceptible to oil. The more volatile oil fractions have a high penetrating power, entering through the seed coat and killing the germ (Plice 1948). In addition, the surface crust that develops after the oil has weathered is a poor seedbed and makes emergence difficult. Competition for available nutrients and oxygen also increases as the activity of decomposers is stimulated by the added carbon source (Gudin and Syrratt 1975; Dibble and Bartha 1979a;

Mitchell et al. 1979). This makes it harder for plants to obtain the nutrients necessary for growth. Oil degradation may also produce toxic reduction products such as hydrogen sulfide gas which may inhibit or restrict plant growth (Bartha 1986).

Many investigators have examined the effects of oil on germination and production. Most of these effects have been negative although some beneficial results have been obtained on oiled soil. Murphy (1929) found that crude petroleum added at a rate of 0.17% by weight to soil delayed germination and reduced biomass by 36%. At a rate of 0.83%, biomass was reduced by 77%. Schwendinger (1968) conducted several laboratory experiments and reported germination of oat seeds was relatively unaffected in a loamy sand with up to 2.9% oil by weight. At 4.9%, however, germination was reduced by 73% when compared to the control. Dry weight biomass for ryegrass was reduced by 28% at an oiling rate of 2.7%. The growth of tomatoes, kale, and leaf lettuce was affected with 1.2% oil by weight in the soil. Uptake of water slowed considerably and the plants began to show typical nutrient deficiencies such as slowing of growth and yellowing of bottom leaves. In a greenhouse study conducted in Nigeria, Udo and Fayemi (1975) reported that germination was reduced 56% in soil oiled at a rate of 6.8% by weight. Plants were dehydrated and stunted. No seeds germinated in soil oiled at a rate of 10.6%. Germination was 100% at oiling rates of 1.1% but yields were only 70% of the control.

Mitchell et al. (1979) planted barley on field plots treated with 10 and 20 liters of oil per square meter. The first year, only 12% of the barley sprouted on the oiled plots versus the unoiled plots. Those

that did sprout on the oiled plots grew only 5 to 10 cm tall compared to the 35 to 55 cm measured on the unoiled plots. The second year the unoiled plots had 5 to 7 times more above ground biomass than the oiled plots. By the end of the fourth year, the 10 liter plots had excellent growth while good growth was underway on the 20 liter plots. In a field study of yields of barley, oats, and wheat, de Jong (1980b) demonstrated that very small amounts of oil caused yield depression. Total above ground biomass was 70% of normal in soil contaminated with 0.05 to 0.25% oil and 43%, 17%, and 13%, for oil levels of 0.51 to 1.0, 2.01 to 4.0, and greater than 4.0%, respectively.

Plice (1948) compared yields of sorghum, cotton, soybeans, and field peas in soils oiled at 0.1, 0.5, and 1.0%. The average yield for the four crops was reduced to 86, 61, and 42%, respectively, of the control at the end of the first growing season. By the end of the third growing season, however, yields on the oiled plots had increased 5, 15, and 20%, respectively, over yields measured for the control plots. The increase in yield was attributed to an increase in nitrogen content on oiled plots from nitrogen in the oil and nitrogen fixation by microbes. Carr (1919) also noted the beneficial effects of oil on plant growth in a greenhouse study of unoiled and oiled soil. At an oiling rate of 0.75% by volume, biomass of soybeans more than doubled when compared to the unoiled pots. A linear relationship between oiling rate and yield was not found; a reduction in yield was noted in soil oiled at a rate of 1.75% when compared to the unoiled pots. At an oiling of 2.25%, no effect on biomass was recorded but biomass was reduced by 64% in soil oiled at a rate of 4% compared to unoiled soil.

Degradation of Crude Oil

As a pollutant, crude oil occupies an intermediate position between highly biodegradable substances and highly recalcitrant substances (Bartha 1986). The extent to which degradation of crude oil occurs and the rate at which the process proceeds is dependent on the type of oil, the nature of the contaminated soil, environmental conditions, and the nature of the microbial community (Dibble and Bartha 1979a; Atlas 1981).

Degradation is defined as the breakdown of petroleum components to compounds of lower molecular weight, or the transformation of petroleum compounds to more polar compounds of a carbon number equal to the parent compound (Atlas 1981). Degradation of oil yields carbon dioxide, water, and organic acids, along with smaller amounts of impurities, insoluble compounds, and microbial biomass (Francke and Clark 1974). High molecular weight, viscosity, and crystallinity are three properties of oil that inhibit biological oxidation and decomposition of oil (Dotson et al. 1970).

Pathways of Degradation

The four main pathways through which natural degradation occurs are evaporation, photo-oxidation, leaching, and biodegradation (Loynachan 1978). Evaporation and photo-oxidation may be minimized in soil systems because petroleum hydrocarbons are subject to rapid vertical infiltration. Bartha (1986) indicated that these two processes may be responsible for only 1 to 2% of the degradation of oil spilled on land. Leaching may also be of little importance in soil

systems. Investigations into the leaching of oil sludges have demonstrated that leachates move only a limited distance in sandy loam and loam soils (Dibble and Bartha 1979b; Skujins and McDonald 1985). Biodegradation, then, remains as the dominant pathway for removal of crude oil contamination from soil.

The ability to biodegrade hydrocarbons is widely distributed among diverse microbial populations (Stone et al. 1942; Cansfield and Racz 1978; Atlas 1981). Over 100 species belonging to 30 genera of bacteria, yeasts, actinomycetes, and fungi present in soil can utilize hydrocarbons ranging from paraffin, kerosene, and gasoline, to asphalts, tars and rubber (Alexander 1961; Dotson et al. 1970; Jobson et al. 1974; Huddleston 1979; Atlas 1981). Microorganisms capable of degrading hydrocarbons are thought to be present in all prairie soils (de Jong 1980a) and are widely distributed in oil field soils, particularly in locations subject to frequent oil pollution (Francke and Clark 1974).

During biodegradation, microorganisms oxidize a portion of the carbon in crude oil for energy, and incorporate a portion into their cell wall (Loynachan 1978). Of the different hydrocarbon fractions present in crude, the straight chain alkane fraction is the most easily degraded by microbes (Stone et al. 1942; Schwendinger 1968; Rowell 1977; Atlas 1981). The rate of decomposition is decreased as the paraffin chain branches or forms ring structures (Schwendinger 1968). Cycloalkanes are particularly resistant to microbial attack and may be impossible to degrade, resulting in an end product of a tar-like residue (Atlas 1977; Atlas 1981). Higher molecular weight compounds

are subject to attack although the rates are much reduced (Schwendinger 1968). Little is known about the degradation of the asphaltic and nitrogen, sulfur, and oxygen fractions. It has been shown, though, that asphaltics tend to increase during biodegradation (Bartha 1986). Dibble and Bartha (1979a) concluded that biodegradation of asphaltic compounds was dependent on the presence of saturated hydrocarbons.

Increasing the Rate of Biodegradation Using Soil Amendments

Early research regarding the removal of oil from soil concluded that natural processes proceeded at very slow rates and that little could be done to remedy the effects of oil unless the oil was completely removed (Knickman 1960 as reported by Schwendinger 1968). Continuing research has discounted this theory and shown that much can be done to enhance the biodegradation of oil in soil.

The process of biodegradation requires sufficient quantities of oxygen, nutrients, and water under favorable conditions of temperature and pH. The rate of biodegradation can be influenced through manipulation of the physical and chemical environment of the soil. Oxygen, nutrients and water can be provided through tillage, fertilization and irrigation to enhance the growth of microorganisms (Jobson et al. 1974; Gudin and Syrratt 1975; Atlas 1977; Dibble and Bartha 1979a; Huddleston 1979; de Jong 1980b; Atlas 1981; Bartha 1986).

Tillage. The presence of free oxygen is essential to biodegradation. Frequent tillage of the soil has been suggested as a practical method to aerate the soil, although the depth of aeration is usually limited to the surface 15 cm by most farm equipment. Loynachan

(1978) monitored carbon evolution from tilled and non-tilled soils contaminated with Prudhoe Bay crude oil. He reported that more carbon was evolved from the disturbed soils than from the undisturbed soils and concluded that tillage should increase oxygen diffusion into the soil or increase hydrocarbon volatilization away from the soil.

Jobson, Cook, and Westlake (1972) reported more rapid degradation of the saturate fraction of two crude oils under conditions of maximum aeration.

Mitchell et al. (1979) found that tillage improved infiltration into oiled plots and was effective in improving yields of barley. Plice (1948) found that tilled plots had naturally revegetated after five years while the non-tilled plots were still bare. Dibble and Bartha (1979b) used a subsoiler to aerate to a depth of 45 cm on an agricultural field contaminated with kerosene. After 21 months, the kerosene in the upper 30 cm had decreased from 0.87% to trace levels. Considerable quantities of oil remained in the 30 to 45 cm zone, however. They concluded that the main factor limiting biodegradation at this depth was reduced aeration.

Fertilization. Many investigators have reported beneficial effects of fertilization. Nitrogen and phosphorus are required in high concentrations for biodegradation to take place at higher rates (Atlas 1977). McGill (1977) developed a nomogram of nitrogen required for several types of oil in soil. The nomogram was developed by considering the amount and type of oil in the soil, and the amount of organic nitrogen available. Other nutrients including sulfur, iron, magnesium, calcium, and sodium are also required but in lesser amounts.

Sandvik, Lode and Pedersen (1986) reported fertilizer stimulated degradation of oily sludge applied to sandy soil. Fertilizer rates of 200, 400, and 600 kg N/ha showed oil reductions of 5, 18, and 22%, respectively, compared to the control in the first nine months and 20, 41, and 51% reduction after 32 months. Kincannon (1972) reported that the rate of biodegradation doubled with the addition of nitrogen and phosphorus. Jobson et al. (1974) found a significant increase in bacterial numbers after the application of nitrogen and phosphorus when compared to soils with no fertilizer. Raymond et al. (1976) found little stimulation of biodegradation by fertilizer in the first eight months after application. Fertilizer did not become a factor until 50% of the added oil was degraded.

Dibble and Bartha (1979a) reported 20 to 24% biodegradation of oil in fertilized soil columns after 120 days as compared to only 10% in the control. Evolution of carbon dioxide (CO_2) was highest for fertilizer rate of 60:1 C:N and a carbon to phosphorus (C:P) ratio of 200:1. Higher levels of fertilization inhibited biodegradation. This same result was also demonstrated by Brown et al. (1981) who measured CO_2 evolution from two different types of separator sludges added to soil. The waste from a petrochemical plant showed optimum degradation at a C:N ratio of 150:1 (adjusted from 350:1). When the C:N ratio was lowered to 20:1, degradation was inhibited. Waste sludge from a refinery had the highest rate of carbon dioxide evolution with the C:N ratio adjusted to 10:1. This rate of degradation was only slightly higher than the control, however, which had a C:N ratio of 110:1. McGill (1977) emphasized that excess nutrient additions can cause

serious deleterious side effects from salinization, excess ammonia, and nitrate contamination of groundwater.

Irrigation. The availability of water is an important limiting factor controlling the rate of biodegradation in soil. Dibble and Bartha (1979c) indicated that oil sludge biodegradation was optimal at soil moisture contents of 30 to 90%. Skujins and McDonald (1985) concluded that, in an arid and semi-arid environment, moisture availability may be critical to biodegradation.

Temperature modification. The effects of temperature on biodegradation are not completely understood and conflicting results have been reported in the literature. Skujins, McDonald, and Knight (1983) found biodegradation took place only during periods of elevated temperatures when studying the landfarming of industrial waste oil. Francke and Clark (1974) noted a similar relationship in a study of the landfarming of waste oil and coolant. Biodegradation proceeded rapidly in warm weather (20 to 22°C) and slowed during cold rainy weather (5 to 15°C). Atlas (1981), on the other hand, reported that Colwell et al. (1978) found higher rates of biodegradation at 3°C than at 22°C in a study of oil contaminated beach sand with mixed microbial cultures. Other studies have shown the optimum temperature for biodegradation to be in the range of 18 to 30°C (Beerstecher 1954; Dibble and Bartha 1979a; Brown et al. 1981; Sandvik et al. 1986). Atlas (1981) concluded that temperature is not a limiting factor except as it affects the physical state of the oil and the availability of water (eg. frozen soils).

In order to modify temperatures in the field, several investigators have utilized plastic sheeting. Gudim and Syrratt (1975) utilized black plastic sheeting to increase soil temperatures on soils contaminated with different types of petroleum hydrocarbons. They documented a higher rate of degradation on plots covered with sheeting than on plots amended with fertilizer and left uncovered.

Liming. The effects of pH on the rate of biodegradation have also been investigated under field and laboratory conditions. A soil pH of 7.0 to 9.0 has been suggested as ideal for both microbial growth and precipitation of any metals which may be associated with the oil (Dibble and Bartha 1979c; Huddleston 1979). Lime is commonly used to adjust soil pH where conditions warrant its use.

MATERIALS AND METHODS

Site Description

The Shay-Wait study site is located in the NW $\frac{1}{4}$ SW $\frac{1}{4}$ NE $\frac{1}{4}$ of Section 24, T.35N., R.2W., Toole County, Montana, at an approximate elevation of 1067 m. The site is situated on rolling upland glaciated plains in north-central Montana (Figure 1). Dryland crop production, oil and gas production, and rangeland are primary land uses in the vicinity of the study area.

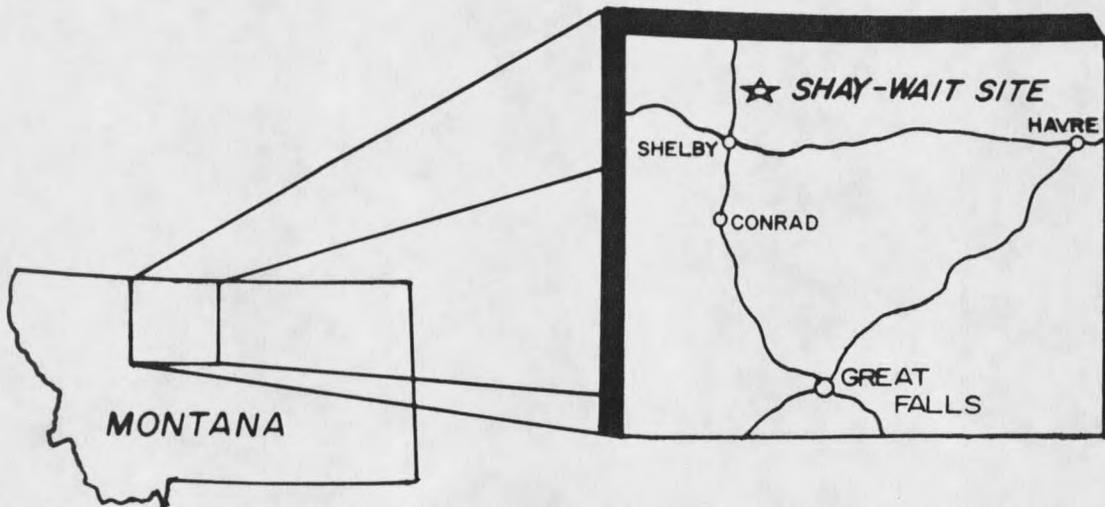


Figure 1. Location of Shay-Wait study site.

Precipitation of 25 to 35 cm per year in this area of the Northern Great Plains supports a shrub and grassland community composed predominantly of Artemisia cana (silver sagebrush), Atriplex spp. (saltbush), Opuntia polyacantha (prickly pear cactus), Artemisia frigida (fringed sagewort), Melilotus officinalis (yellow sweetclover),

Agropyron smithii (western wheatgrass), Bouteloua gracilis (blue gramma), Stipa comata (needleandthread), and Poa spp. (bluegrass). Other plants noted on the site included Ceratodites lanata (winterfat) and Gutierrezia sarothrae (broom snakeweed). Average monthly temperature and precipitation measured at the Chester, Montana weather station (42 miles SE of the study site) are shown in Figure 2. Total precipitation for the 10½ month study period was 11.81 cm.

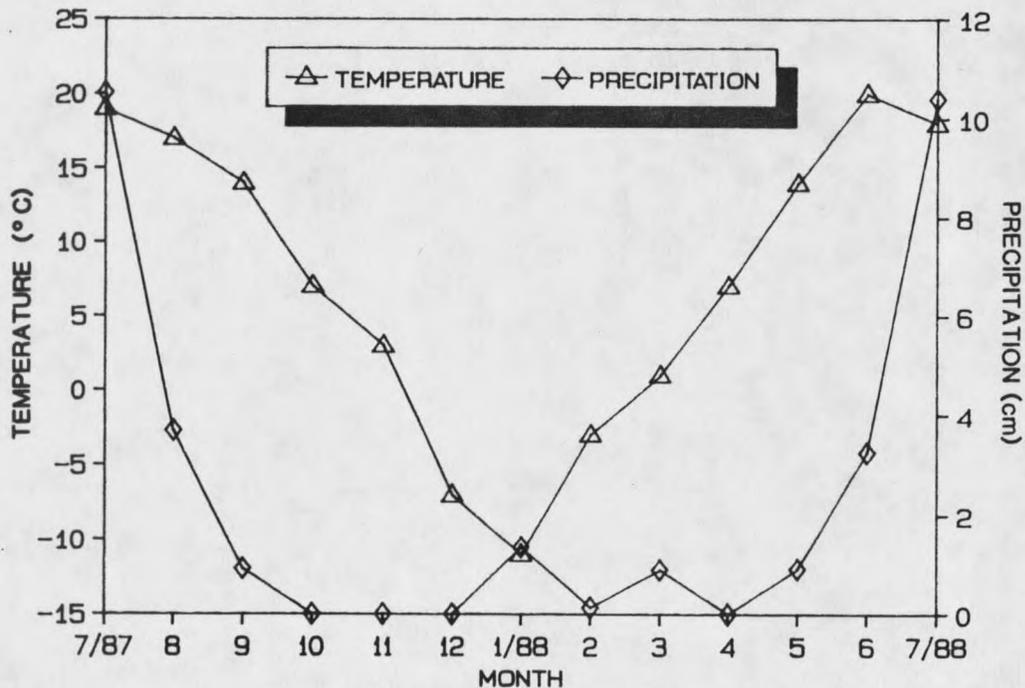


Figure 2. Average monthly temperature and precipitation.

Soils in the area are predominantly sandy loam and clay loam in texture. They are developing on a thin mantle of glacial till (2 to 6 meters thick) which overlies bedrock composed of dark grey to black Colorado Shale. The soil profile is 1 to 1.25 m thick and is classified by the Soil Conservation Service as a fine, montmorillonitic Borollic Natrargid belonging to the Creed Series.

The Shay-Wait site lies within the boundaries of the Kevin-Sunburst Oil Field. In 1923, an oil well was drilled on this location to a depth of 459 m into the Madison Formation (State of Montana Oil and Gas Conservation Commission records). The site was believed to be contaminated with oil released from an oil storage pit which overtopped its enclosing berm. This oil spread along a gentle gradient to the southwest of the pit for approximately 150 m covering an area approximately 0.31 ha in size. Although the exact age of the spill cannot be determined, it was identified on an aerial photograph taken in 1951.

Shrubs and grasses (especially western wheatgrass) are actively growing in the oiled soils on a large portion of the contaminated area. Approximately 0.09 ha of the total area contaminated is barren of vegetation except for isolated tufts of Hordeum jubatum (foxtail barley). It is not known if all of the existing vegetation was present at the time of the spill and was not affected by the oil or whether these plants have naturally revegetated the site after the initial contamination.

The chemical composition of the weathered oil contaminating the Shay-Wait site was not determined for this study. The chemical composition of an oil produced from the same formation in a nearby well is listed in Table 1. The oil is described as brownish-green in color with a specific gravity of 0.877 and a sulfur content of 1.12% (Tomnsen

Table 1. Chemical composition of Madison oil.

Distillate Fraction	Composition (% by volume)
Light gasoline	4.5
Total gas and naphtha	20.2
Kerosene distillates	5.1
Gas oil	16.4
Non-viscous lube distillate	13.2
Medium lube distillate	9.7
Viscous lube distillate	2.3
Residue	29.0
Carbon residue (by weight)	2.5

1985). The fractions remaining in the soil at the Shay-Wait site probably include residue (asphaltic fraction), lube distillates, and gas oil.

Preliminary Soil Sampling

A preliminary survey of the site was conducted in July of 1987 to characterize the distribution of oil in the soil and obtain baseline soil data. Nine soil samples were taken with a 5 cm Shelby tube sampler to a depth of 122 cm. Each sample was made up of three subsamples taken from within a 1.2 m radius of a staked sampling point and divided into four depth increments: 0 to 5, 5 to 15, 15 to 46, and 46 to 122 cm. Seven of the samples were taken from non-vegetated areas below the oil storage pit, one from the oil storage pit, and one from a vegetated contaminated soil.

A single soil sample from each depth increment was analyzed for 16 parameters (Table 2). This sample was made up of a composite of the seven samples taken from the non-vegetated area below the oil storage pit. These data indicate that the oil was predominantly located in the

Table 2. Soil characteristics of the Shay-Wait site.

Parameter	Sample Depth (cm)				Method of Analysis*
	0-5	5-15	15-46	46-122	
Texture	sandy loam	loam	clay loam	loam	{1}, 43-5
Extractable Oil (% wt)	5.0	0.95	0.2	0.07	{2}, 503
SAR	16	16	33	32	{3}, 20b
EC (mmhos·cm ⁻¹)	2.6	2.0	3.6	4.5	{3}, 3a,4b
pH	7.1	7.4	8.3	8.5	{3}, 21a
CEC (meq·100 g ⁻¹)	14.5	16.0	21.5	19.9	{1}, 57-2
Organic Carbon (ppm)	76000	25000	9300	5800	{1}, 90-3
Total N (ppm)	1678	1041	917	622	{1}, 83-3
Nitrate-N (ppm)	<1	2	2	5	{1}, 84-2
C/N ratio	45:1	24:1	10:1	9:1	
Available P (ppm)	10	16	12	11	{1}, 73-4
Available K (ppm)	385	362	445	223	{1}, 71-3
Arsenic (ppm)	0.32	0.16	0.09	0.18	{1}, 80-3
Cadmium (ppm)	0.1	<0.1	<0.1	<0.1	{4}, p.600
Chromium (ppm)	<0.1	<0.1	<0.1	<0.1	{4}, p.600
Lead (ppm)	1.7	1.2	1.7	1.2	{4}, p.600

- *{1} Black. 1965. Methods of Soil Analysis, ASA Monograph No. 9.
 {2} Franson et al. 1976. Standard Methods for the Examination of Water and Wastewater.
 {3} Richards. 1954. Diagnosis and improvement of saline and alkali soil. Agricultural Handbook No. 60.
 {4} Follett and Lindsay. 1971. Changes in DTPA-extractable zinc, iron, manganese, and copper in soils following fertilization.

upper 46 cm of the soil profile. The highest oil content was in the 0 to 5 cm interval (5% oil). Soil oil content decreased substantially with depth to a minimum concentration in the 46 to 122 cm interval. Soil oil content in the oil storage pit was 7.2% in the top 15 cm. Oil content in the sample taken from the vegetated area was 4.2% in the top 10 cm.

The sodium adsorption ratio (SAR) of the soil was high at all depths and doubled in value between the 5 to 15 and 15 to 46 cm interval. The soil is classified as sodic (SAR > 13) and also exhibits the presence of a natric horizon below a depth of 15 cm (SAR > 15).

Columnar structure was observed in two soil cores and in one shallow pit between 10 and 15 cm. The pH of the soil was neutral in the surface 15 cm. The pH became alkaline below 15 cm reflecting the increase in sodium content.

The texture of the soil was sandy loam to clay loam and had a cation exchange capacity (CEC) of 14.5 to 21.5 meq·100 g⁻¹. Other notable chemical characteristics of the soil were high C:N ratios, slightly saline to saline electrical conductivities (EC), and low nitrate-N levels. Phosphorus (P) and potassium (K) were both in the range considered high for range soils (Donahue et al. 1983). The four metals arsenic, cadmium, chromium, and lead were all at levels considered non-phytotoxic (Adriano 1986; EPA 1987).

Experimental Design and Treatment Installation

Ten treatments were chosen to be tested in a randomized complete block design with three replications (Figure 3). Plot size was 2 m by 2 m. The treatments were determined by first considering methods proven effective in enhancing the physical and chemical soil environment for microbial degradation. Ease of implementation with equipment and resources readily available to local landowners was also considered. The treatments tested are listed in Table 3.

Soils were sampled four times during a 10½ month period beginning August 27, 1987 and ending July 12, 1988. The first sampling took place prior to treatment application. Two cores were taken from each plot to a depth of 46 cm using a hand driven 5 cm Shelby tube core

Figure 3. Plan view of experimental design.

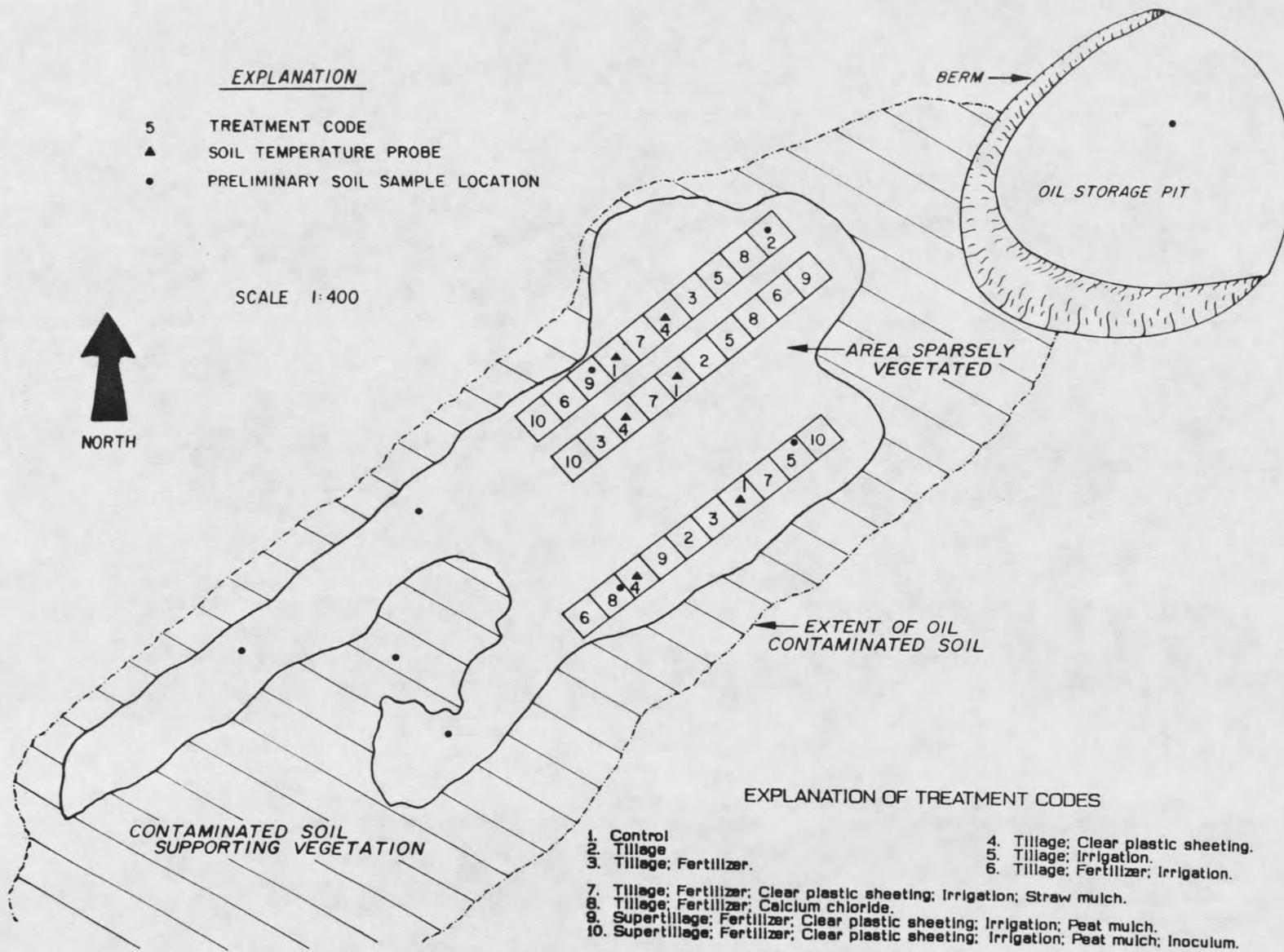


Table 3. Treatments applied to Shay-Wait plots.

Treatment Number	Treatment
1	Control
2	Tillage
3	Tillage; Fertilizer.
4	Tillage; Clear plastic sheeting.
5	Tillage; Irrigation.
6	Tillage; Fertilizer; Irrigation.
7	Tillage; Fertilizer; Clear plastic sheeting; Irrigation; Straw mulch.
8	Tillage; Fertilizer; Calcium chloride.
9	Supertillage; Fertilizer; Clear plastic sheeting; Irrigation; Peat moss mulch.
10	Supertillage; Fertilizer; Clear plastic sheeting; Irrigation; Peat moss mulch; Inoculum.

sampler. Each core was divided into three increments (0 to 5, 5 to 15, and 15 to 46 cm) and composited with the same depth interval from the other core in a plastic bucket.

All plots except the control were then tilled with a tractor mounted rototiller. Rototilling was effective to a depth of 15 to 20 cm. Plots that were supertilled were rototilled as above and then tilled with a rotary flailer implement designed to break soil clods into smaller aggregates. All tilled plots were then chiseled with a ripping bar by making four passes spaced approximately 30 cm apart. The depth of chiseling was effective to between 30 and 45 cm. After chiseling, the plots were retilled with the rototiller.

Plots receiving fertilizer were individually fertilized with a premeasured amount of an N-P-K mixture. Each plot received 448 kg/ha N in the form of 75% urea (45-0-0) and 25% ammonium nitrate (34-0-0), 93 kg/ha P₂O₅ as monoammonium phosphate (11-52-0), and 56 kg/ha K₂O as potassium chloride (0-0-60).

Calcium chloride (CaCl_2) flakes were applied to designated plots at a rate of 9.84 mtons/ha. This rate was designed to replace 1.5 meq of sodium on the cation exchange sites of colloidal particles to a depth of 30 cm, reducing the exchangeable sodium percentage (ESP) from 16 to 6. The rate was calculated according to the following formula:

$$2.52 \text{ mton} \cdot \text{ha}^{-1} \text{ CaCl}_2 \cdot (\text{meq Na})^{-1} \times 1.5 \text{ meq Na} \\ \times 1.25 \div 0.96$$

The value 1.25 represents a lack of quantitative displacement. Since the calcium chloride was only 96% pure, the equation was divided by 0.96. The resulting number was arbitrarily doubled to account for potential hydrocarbon interference due to the possibility that oil coating the soil particles could interfere with the exchange of calcium for sodium on the cation exchange sites.

Straw and peat moss organic amendments were applied at a rate of 4.5 mton/ha. The inoculum applied to Treatment 10 was composed of a mix of three species: Phanerochaete chrysosporum, Fusarium oxysporum, and Pleurotus ostreatus. The organisms were preserved in an aqueous nutrient solution and applied to the soil with a hand held spray gun at a rate of 700 ml per plot (2.13×10^7 organisms cm^{-2}).

All the amendments were incorporated into the soil with a hand operated rototiller. After incorporation, plots were resampled as previously described. Designated plots were irrigated with tap water at a rate of 2.5 cm per plot. Irrigation was expected to bring soil moisture levels to field capacity in the top 15 cm of soil. Six mil clear plastic sheeting was used to cover plots receiving temperature modification. The plastic was stapled to a wooden frame and anchored

with stone cobbles. Numerous holes 0.5 cm in diameter were opened in the plastic to allow exchange of gases and moisture.

Soils were resampled at the end of 205 days and again after 315 days. The 205 day sampling was conducted in the manner described previously except the subsamples were analyzed separately for oil content to determine subsample variation. The sampling procedure was slightly altered for the next sampling at 315 days after treatment when a 2 cm Oakfield sampler was used instead of the 5 cm Shelby tubes used previously. The number of subsamples was also increased for this sampling to five for the 0 to 5 and 5 to 15 cm depth intervals.

Field Measurements

Infiltration

Infiltration was measured in the field after the 315 day sampling. Infiltration rates were determined with double ring infiltrometers in the manner suggested by Haise et al. (1956) and Johnson (1963). The inner ring was a steel cylinder 15.2 cm in diameter with an outer ring constructed of galvanized tin 35.6 cm in diameter. The rings were driven 10 cm into each plot and then filled with water to maintain a head of 10 cm above the ground surface. Readings were taken at 5, 10, 15, 30, 45, 60 and 90 minutes by measuring the volume of water needed to fill the inner ring to the 10 cm head level. Water was added to the outer ring at the same time to maintain the 10 cm head.

Temperature Monitoring

Thermocouple thermometers were installed in the control (Treatment 1) and tillage-clear plastic sheeting (Treatment 4) in each block for

the purpose of monitoring temperature differences between the two treatments. The thermometers were placed inside a 1.25 cm pvc tube at 2, 10, 25, and 50 cm from the top of the tube and sealed. The tubes were then buried upright in each plot. Soil temperature was measured periodically during the 10½ month study period with an Omega Type T digital thermometer.

Analytical Methods

Soil Sample Preparation

Soil samples were transferred to the laboratory in iced coolers where they were stored at 4°C. Preparation included air drying, disaggregation with a mechanical flailer, and sieving through a 2 mm mesh screen. After preparation, the soils were permanently stored at 4°C.

Oil Extraction

Oil content was measured using a vacuum extraction gravimetric method. This method was adapted from one used by Brown et al (1981) and a gravimetric method used for determination of oil and grease in water samples (Franson, Rand, Greenberg, and Taras 1976). Freon (1,1,2 trichloro 1,2,2 trifluoroethane) was chosen as the solvent because it is relatively safe to handle and innocuous to human health. Freon efficiently extracts most middle weight hydrocarbons but will not break down some heavier asphaltics and will solubilize some organic compounds and fats. Freon has a boiling point of 47°C and evaporates at a lower temperature than most of the hydrocarbons thought to be present in the Shay-Wait soils.

The extraction procedure entailed weighing out 25 grams of soil into a 125 ml Erlenmeyer flask. Twenty-five ml of Freon was added to the flask, the flask shaken, and then allowed to stand for 30 minutes. The sample was then transferred to an 80 ml Coors Buchner funnel fitted with a 5.5 cm number 42 Whatman filter paper. The funnel was placed into a teflon stoppered 500 ml filtering flask connected to a vacuum pump. A 60 ml test tube placed inside the filtering flask was used to collect the filtrate. After the soil was extracted, the test tube containing the filtrate was transferred into a preweighed 125 ml Erlenmeyer flask. The soil in the funnel was washed three more times with 25 ml aliquots of Freon. After all filtrates had been transferred, the flask was put into a water bath at 55°C for 7 hours. The flask was then dried in a desiccator for 30 minutes and the weight of the residue determined.

The precision of the method was determined with five replications of a representative sample. The average oil content of the sample was 1.259 gm oil (5.04% by weight) with a standard deviation of 0.031 grams. The coefficient of variation was 2.4%.

Fertility

Fertility was initially determined by analyzing soils for nitrate-N (NaCl extraction), phosphorous (NaHCO₃ extraction), and potassium (NH₄Ac extraction). Standard methods 84-2 (Bremner 1965), 73-4 (Olsen and Dean 1965), and 71-3 (Pratt 1965), respectively, were followed. Since both phosphorous and potassium were considered to be in the high to very high range for prairie soils (Donahue et al. 1983), only nitrate-N was measured in the 315 day samples. A Technicon Auto-

Analyzer 1 was used for determination of nitrate-N for this sampling (Sims and Jackson 1971).

Statistical Analysis

Analysis of variance (ANOVA) was performed on extracted oil values. The Least Significant Difference (LSD) method of multiple comparisons was used to test differences between treatments only if the F value (ratio between mean square treatments and mean square error) was significant. This is known as Fischer's least significant difference (Carmer and Walker 1985). Since no correlation was found between initial oil content and change in oil content after 315 days ($r^2 = .00, .44, \text{ and } .47$ for the 0 to 5, 5 to 15, and 15 to 46 cm intervals, respectively), ANOVA between treatments was determined by testing the amount of change in soil oil content between sampling dates. A significance level of 0.05 was used to determine all differences. The three depth intervals were considered as independent data sets and analyzed separately.

Comparison contrasts were also used to analyze changes in soil oil content. Contrasts group treatments sharing a common amendment or amendments together, and compare them against the group of remaining treatments. This procedure simplifies the experimental design by reducing the number of treatments to two. For example, fertilized treatments were tested against non-fertilized treatments for significant changes in soil oil content. A Student's t-statistic is used for the test of significance.

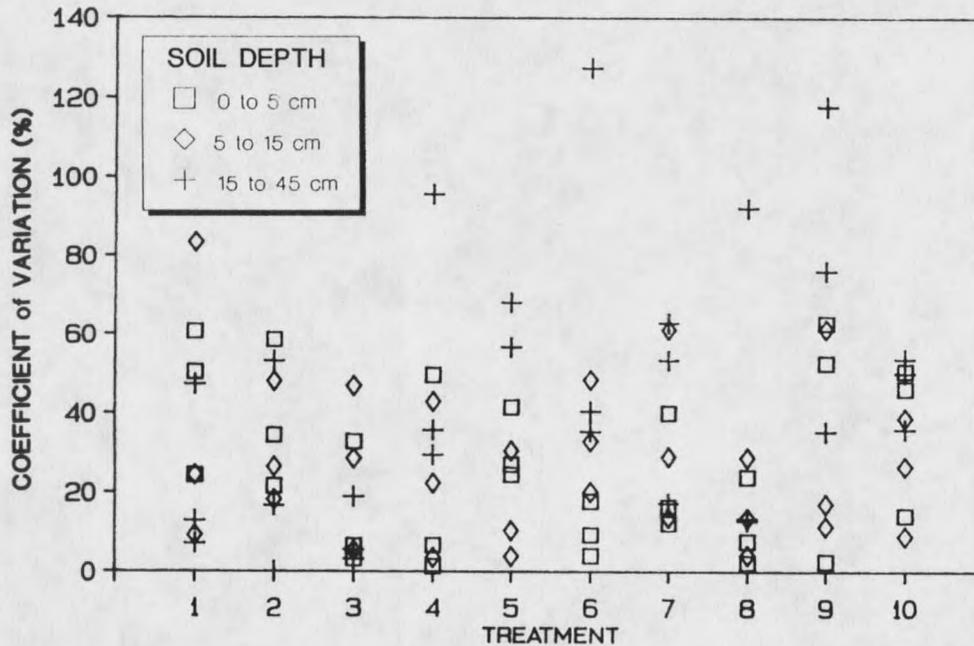
Statistical tests were also used for fertility, infiltration, and temperature data. The comparison contrasting method was used to test differences in fertility between treatments. The Student's t-statistic was used to test differences in temperature between plastic covered and non-plastic covered plots. The LSD multiple comparison was used to test differences in infiltration rate between treatments.

RESULTS AND DISCUSSION

Experimental Error

The randomized complete block design partitions the sum of squares from the analysis of variance (ANOVA) into three main sources of variation: between blocks, between treatments, and block by treatment interaction. The third term, block by treatment interaction, contains deviations from expected values which are commonly referred to as error. The precision of the experimental design is determined by the value of this term in relation to the value of treatment variation. As the amount of variation in soil oil content increases, the ability of the design to detect treatment differences decreases.

The error term can be further partitioned into sampling and analytical error. At the Shay-Wait site, the largest proportion of sampling error was introduced by the variation between subsamples taken in individual plots. Subsamples from the 205 day sampling were analyzed separately (instead of composited) for oil content to determine the subsampling coefficient of variation (Figure 4). The coefficient of variation measures the percent deviation from the mean of the two samples. Average variation was 27% for the 0 to 5 and 5 to 15 cm intervals and 44% for the 15 to 46 cm interval. Values range from a minimum of 0 to a high of 127%. High variation in subsamples indicates a heterogeneous distribution of oil. In order to reduce



EXPLANATION OF TREATMENT CODES

- | | |
|---|-------------------------------------|
| 1. Control | 4. Tillage; Clear plastic sheeting. |
| 2. Tillage | 5. Tillage; Irrigation. |
| 3. Tillage; Fertilizer. | 6. Tillage; Fertilizer; Irrigation. |
| 7. Tillage; Fertilizer; Clear plastic sheeting; Irrigation; Straw mulch. | |
| 8. Tillage; Fertilizer; Calcium chloride. | |
| 9. Supertillage; Fertilizer; Clear plastic sheeting; Irrigation; Peat mulch. | |
| 10. Supertillage; Fertilizer; Clear plastic sheeting; Irrigation; Peat mulch; Inoculum. | |

Figure 4. Coefficients of variation calculated from extracted oil values measured in soil samples collected 205 days after treatment.

variation, the number of subsamples composited per plot was increased to five for the 315 day sampling.

Analytical error is reduced in the laboratory by using standard references and duplicating sample analysis. No standard reference was available for the particular oil present at the Shay-Wait site, but the coefficient of variation for the initial calibration of the extraction procedure was 2.4%. A duplicate analysis was run on every ninth sample. The average coefficient of variation for all duplicates was 4.6%.

Soil Oil Content

Filtering of the oil with depth as discussed by Plice (1948) was visually apparent. Oil extracted from the 0 to 5 cm interval was black, changing to dark brown in the 5 to 15 cm interval, and to bright gold in the 15 to 46 cm interval. These colors correspond to the heavier asphaltic fraction remaining near the surface while the lighter fractions moved to greater depths. A noticeable decrease in viscosity of the extracted oil was evident in the 15 to 46 cm interval.

Soil Oil Content in the 0 to 5 cm
Depth Interval

Considerable variation in pretreatment oil levels was measured in the 30 plots sampled in the 0 to 5 cm interval. The range extended from a high of 9.28 to a low of 1.29 percent oil (Table 4). The average oil content for all plots was 5.20 percent with a standard deviation of 2.27. Soil oil content for each treatment varied somewhat less, as pretreatment averages ranged from 7.14 to 3.31 percent. These values are tabulated in Table 5 and illustrated in Figure 5.

Table 4. Summary statistics of soil oil in the 0 to 5 cm depth interval.

Sampling	Average Soil Oil Content (% by weight)					
	Mean	Std Dev*	Skewness	Kurtosis	Min*	Max*
Pretreatment	5.20	2.27	0.28	2.20	1.29	9.28
1 day	2.18	1.51	1.40	4.30	0.70	6.62
205 days	2.20	1.71	1.33	3.63	0.68	6.85
315 days	2.18	1.69	1.77	5.27	0.66	7.01
1 day change	-3.02	2.12	-0.49	2.65	-7.64	0.00
205 day change	0.02	0.54	0.39	3.28	-1.26	1.16
315 day change	0.00	0.74	1.74	8.38	-1.42	2.81

* Std Dev = Standard deviation; Min = minimum; Max = maximum.

Table 5. Changes in soil oil content in the 0 to 5 cm depth interval.

Treatment	Average Soil Oil Content (% oil by weight)				Change in Soil Oil Content (% oil)*		
	Pretreatment	1 day	205 days	315 days	1 day	205 days	315 days
1	4.00	4.00	4.28	5.28	0.00	0.28 cb**	1.28
2	3.31	1.02	0.96	1.05	-2.29	-0.06 ab	0.03
3	5.46	3.11	2.90	2.76	-2.35	-0.21 ab	-0.35
4	5.18	2.94	2.86	2.51	-2.24	-0.08 ab	-0.43
5	4.59	1.05	0.97	1.08	-3.54	-0.08 ab	0.03
6	7.14	1.41	2.27	1.94	-5.73	0.86 c	0.53
7	5.27	2.05	2.35	1.83	-3.22	0.30 cb	-0.22
8	6.81	2.40	1.67	1.87	-4.41	-0.73 a	-0.53
9	4.55	1.19	1.19	0.96	-3.38	0.00 b	-0.23
10	5.70	2.62	2.57	2.54	-3.08	-0.05 ab	-0.08

* Change for 1 day values calculated by subtracting 1 day from pre-treatment oil content. Change for 205 and 315 day values calculated by subtracting from 1 day oil content value.

** Letters indicate significant difference sets using LSD. Treatments sharing a common letter are not significantly different. Columns without letters had no significant differences between treatments.

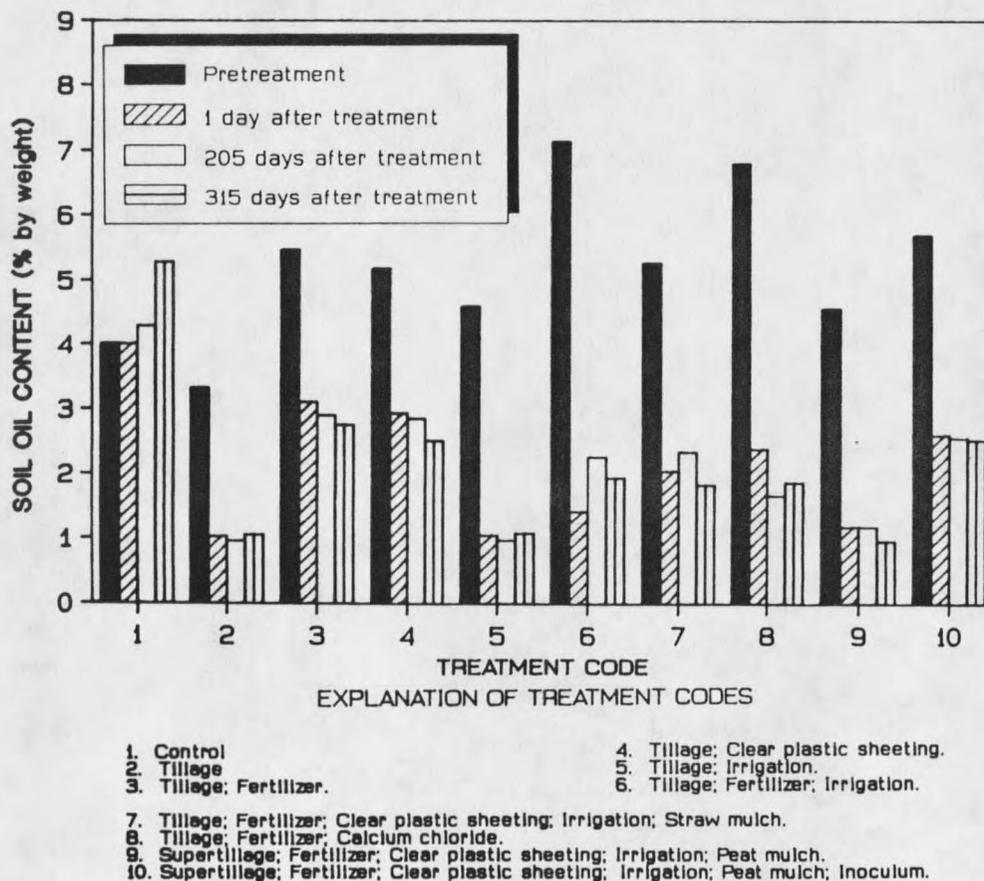


Figure 5. Average soil oil content in the 0 to 5 cm depth interval.

Soil oil content was greatly reduced in the 0 to 5 cm interval one day after treatment application (hatched bar in Figure 5). This decrease is attributable to the operation of tillage. Tilling the soil effectively mixed the oil from the surface 5 cm to a depth of approximately 15 to 20 cm. Oil content dropped an average of 3.36 percent oil, a 65% reduction, in the nine treatments that were tilled. Tillage was also effective in reducing the heterogeneity of oil distribution in the plots as shown by the drop in the standard deviation of the average oil content from 2.27 to 1.51 (Table 4). Since tillage was the only amendment influencing soil oil content at this sampling, a statistical analysis of the significance of tillage was computed by pooling the nine treatments tilled and testing them against the control. The ANOVA showed that tillage significantly reduced soil oil levels.

By the 205 day sampling, both increases and decreases were recorded in soil oil content (white bar in Figure 5). The overall average oil level increased slightly to 2.20 percent versus an average of 2.18 percent by weight recorded for the one day sampling. An increase in oil level was recorded for the control (Treatment 1), tillage-fertilizer-irrigation (Treatment 6), and tillage-fertilizer-irrigation-plastic sheeting-straw mulch (Treatment 7). The small increase in soil oil measured in the control and Treatment 7 is probably due to the heterogenous distribution of oil in each plot sampled. As shown in Figure 4, the subsample coefficient of variation for the control was 61, 50, and 24% for the three replicates. The increase in soil oil exhibited by Treatment 6 may be due to the

production of more freon extractable oil during the period between sampling dates. This interpretation is supported by the large increase in soil oil content (61%) in conjunction with a low subsample coefficient of variation (4 to 18%; see Figure 4) for the three replications. The ANOVA for the difference in oil levels between the 205 day and one day samples showed that tillage-fertilizer-CaCl₂ (Treatment 8) had a significantly greater decrease than the control. This was the only treatment to be significantly different than the control. The calcium chloride treatment also exhibited the largest decrease in oil content of all the treatments (0.73 percent oil by weight). This decrease was probably due to improved flocculation of colloidal particles caused by the exchange of calcium ions for sodium ions on the cation exchange sites. This in turn resulted in a higher relative flux of water and oxygen into the soil.

The 315 day sampling revealed little change in soil oil content. The most notable changes occurred in the control (Treatment 1), tillage-fertilizer-irrigation (Treatment 6), and tillage-fertilizer-CaCl₂ (Treatment 8). The large increase in oil content for the control could only be attributed to the heterogeneous distribution of oil in the control plots. Oil levels for Treatment 6 decreased 14% below levels measured in the 205 day samples. Oil content for Treatment 8 increased 12% over the 205 day level but decreased overall 22%, the largest decrease of all the treatments. No treatment had significantly lower oil levels than the control in the period between the 315 and one day samplings.

Soil Oil Content in the 5 to 15 cm
Depth Interval

Pretreatment oil levels in the 5 to 15 cm interval varied from a high of 8.36 to a low of 0.14 percent by volume in the 30 plots sampled (Table 6). The overall average was 1.40 percent oil with a standard deviation of 1.72. Pretreatment averages for the treatments varied from 3.77 to 0.68 percent oil by weight. These data are tabulated in Table 7 and illustrated in Figure 6. An ANOVA of pretreatment soil oil content showed no significant differences between treatments.

Table 6. Summary statistics of soil oil in the 5 to 15 cm depth interval.

Sampling	Average Soil Oil Content (% by weight)					
	Mean	Std Dev*	Skewness	Kurtosis	Min*	Max*
Pretreatment	1.41	1.72	2.75	10.85	0.14	8.36
1 day	1.93	1.34	0.91	2.81	0.26	5.49
205 days	1.74	1.36	1.55	5.21	0.14	6.03
315 days	1.34	1.01	2.03	8.13	0.25	5.22
1 day change	0.52	1.36	0.08	3.82	-2.87	3.69
205 day change	-0.18	0.73	0.67	4.61	-1.65	2.05
315 day change	-0.59	0.76	-1.33	5.02	-3.02	0.71

* Std Dev = Standard deviation; Min = Minimum; Max = Maximum.

Soil oil content for the one day sampling is indicated by the hatched bar in Figure 6. Oil levels increased an average of 0.58 percent oil, a 41% increase in oil content. This increase is attributed to tillage, which mixed oil from the surface into this interval. Again, tillage was effective in reducing the heterogeneity of oil distribution in the plots, indicated by the drop in the standard deviation of the average oil content by 0.37 percent oil (Table 6).

Table 7. Changes in soil oil content in the 5 to 15 cm depth interval.*

Treatment	Average Soil Oil Content (% oil by weight)				Change in Soil Oil Content (% oil)**		
	Pretreatment	1 day	205 days	315 days	1 day	205 days	315 days
1	0.68	0.68	0.36	0.48	0.00	-0.32	-0.20
2	0.84	0.95	1.13	0.58	0.11	0.18	-0.37
3	3.77	2.81	2.81	2.46	-0.96	0.00	-0.35
4	1.86	3.07	3.24	1.94	1.21	0.17	-1.13
5	0.83	1.17	0.96	0.80	0.34	-0.21	-0.37
6	1.29	2.23	1.83	1.30	0.94	-0.40	-0.93
7	0.94	2.35	2.13	1.49	1.41	-0.22	-0.86
8	0.44	2.28	2.07	1.36	1.84	-0.21	-0.92
9	0.72	0.91	0.83	1.01	0.19	-0.08	0.10
10	2.67	2.82	2.09	1.98	0.15	-0.73	-0.84

* No significant differences existed between treatments for this data set.

** Change for 1 day values calculated by subtracting 1 day from pre-treatment oil content. Change for 205 and 315 day values calculated by subtracting from 1 day oil content value.

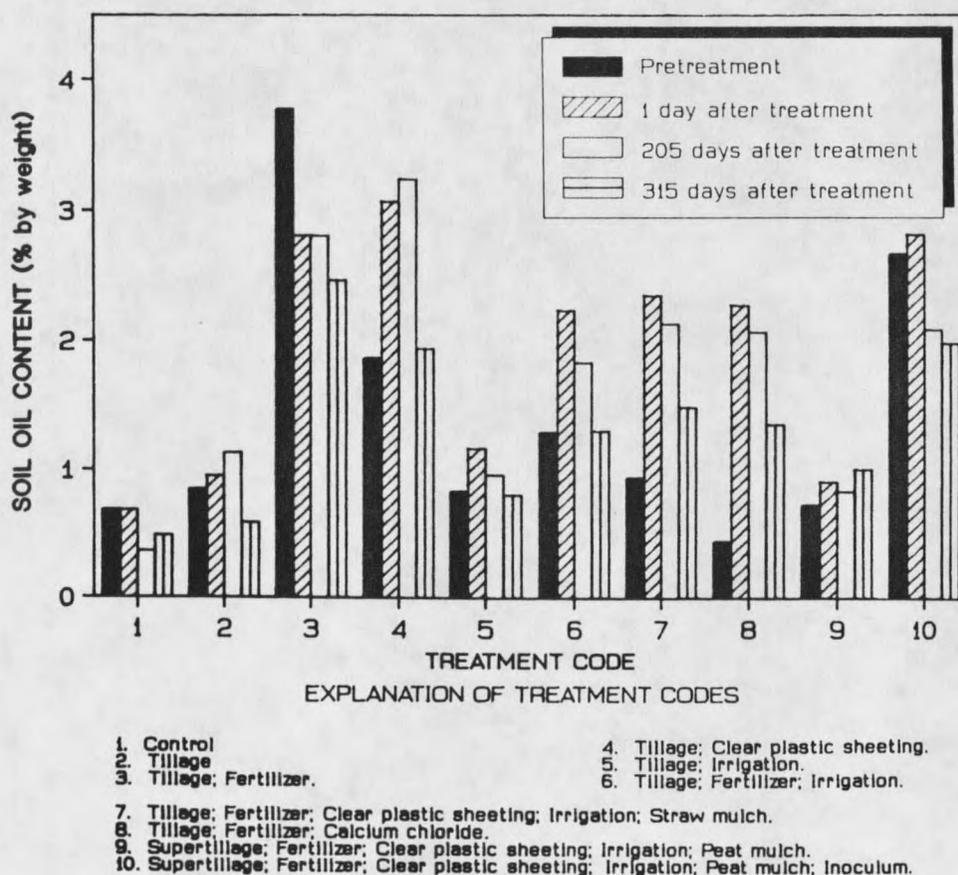


Figure 6. Average soil oil content in the 5 to 15 cm depth interval.

Soil oil content for the 215 day sampling is indicated by the white bar in Figure 6. Oil content was slightly lower than the previous sampling for most of the treatments. Two treatments showed increases in oil content. Tillage-plastic sheeting (Treatment 4) increased by 6% and tillage (Treatment 2) increased by 19%. The average reduction for all treatments was 10%. An ANOVA indicated that none of these changes were significantly different than the control (Treatment 1), which decreased 47%. The large decrease by the control was, again, probably due to variation in soil oil content present in the control plots. Figure 4 shows coefficients of variation for the 5 to 15 cm control subsamples to be 83, 24, and 9% for the replications.

Oil content was lower for all treatments in the 315 day soil samples except for the control (Treatment 1) and supertillage-fertilizer-plastic sheeting-irrigation-peat moss mulch (Treatment 9). These two treatments increased in oil content above previous levels by 33 and 21%, respectively. Overall, an average decrease of 0.58 percent oil (30% reduction) was measured for all treatments (Table 6), returning oil levels to the pretreatment average of 1.40 percent oil.

Soil Oil Content in the 15 to 46 cm Depth Interval

Pretreatment average oil content in the 15 to 46 cm interval was 0.41 percent with a standard deviation of 0.50 (Table 8). A maximum of 2.44 and a minimum of 0.02 percent oil was extracted from the plots. Treatment averages (Table 9 and Figure 7) varied from 1.01 to 0.08% oil.

Table 8. Summary statistics of soil oil in the 15 to 46 cm depth interval.

Sampling	Average Soil Oil Content (% by weight)					
	Mean	Std Dev*	Skewness	Kurtosis	Min*	Max*
Pretreatment	0.41	0.49	2.63	10.68	0.02	2.44
1 day	0.28	0.42	3.85	18.59	0.01	2.31
205 days	0.29	0.46	4.30	21.92	0.04	2.58
315 days	0.29	0.69	4.88	25.91	0.01	3.91
1 day change	-0.13	0.26	-2.18	9.11	-1.19	0.21
205 day change	0.01	0.14	0.04	3.36	-0.31	0.36
315 day change	0.01	0.33	3.67	19.10	-0.50	1.60

* Std Dev = Standard deviation; Min = Minimum; Max = Maximum.

Table 9. Changes in soil oil content in the 15 to 46 cm depth interval.*

Treatment	Average Soil Oil Content (% oil by weight)				Change in Soil Oil Content (% oil)**		
	Pretreatment	1 day	205 days	315 days	1 day	205 days	315 days
1	0.21	0.21	0.10	0.09	0.00	-0.11	-0.12
2	0.08	0.16	0.11	0.16	0.08	-0.05	0.00
3	1.01	0.93	1.03	1.46	-0.08	0.10	0.53
4	0.46	0.46	0.47	0.40	-0.00	0.01	-0.06
5	0.25	0.13	0.08	0.11	-0.12	-0.05	-0.02
6	0.56	0.10	0.17	0.18	-0.46	0.07	0.08
7	0.50	0.24	0.28	0.17	-0.26	0.04	-0.07
8	0.11	0.12	0.16	0.06	0.01	0.04	-0.06
9	0.20	0.08	0.14	0.07	-0.12	0.06	-0.01
10	0.74	0.33	0.36	0.16	-0.41	0.03	-0.17

* No significant differences existed between treatments for this data set.

** Change for 1 day values calculated by subtracting 1 day from pre-treatment oil content. Change for 205 and 315 day values calculated by subtracting from 1 day oil content value.

EXPLANATION OF TREATMENT CODES

- | | |
|---|-------------------------------------|
| 1. Control | 4. Tillage; Clear plastic sheeting. |
| 2. Tillage | 5. Tillage; Irrigation. |
| 3. Tillage; Fertilizer. | 6. Tillage; Fertilizer; Irrigation. |
| 7. Tillage; Fertilizer; Clear plastic sheeting; Irrigation; Straw mulch. | |
| 8. Tillage; Fertilizer; Calcium chloride. | |
| 9. Supertillage; Fertilizer; Clear plastic sheeting; Irrigation; Peat mulch. | |
| 10. Supertillage; Fertilizer; Clear plastic sheeting; Irrigation; Peat mulch; Inoculum. | |

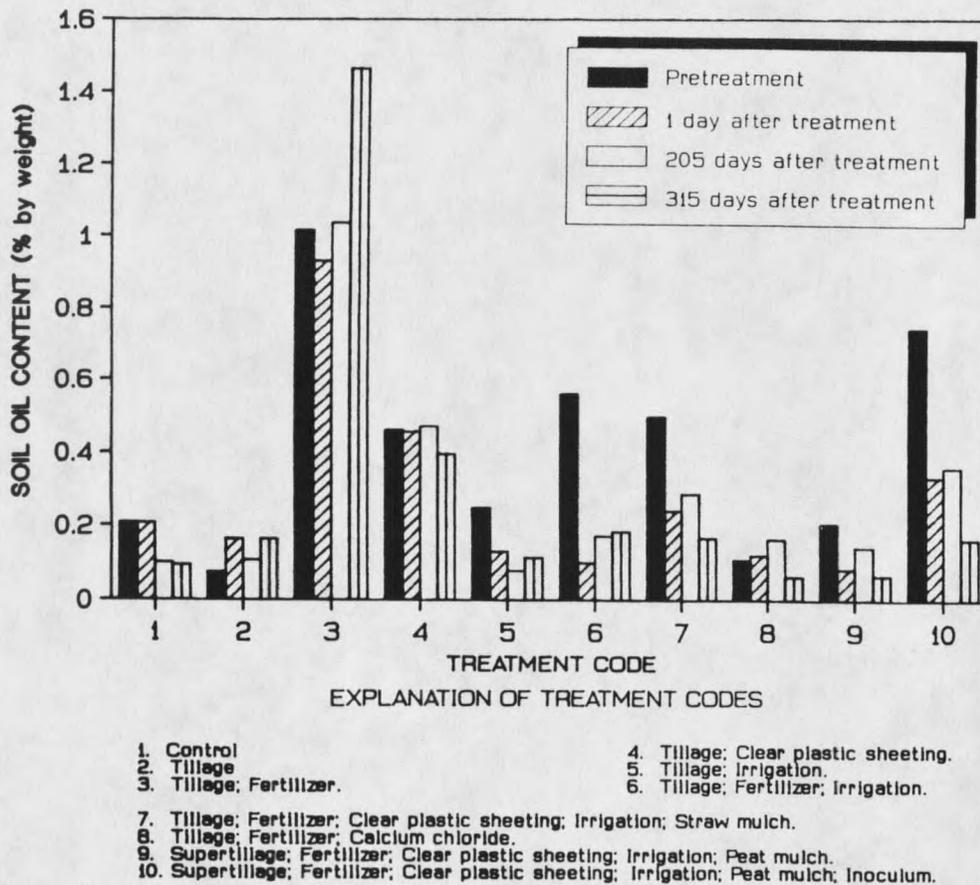


Figure 7. Average soil oil levels by treatment in the 15 to 46 cm depth interval.

Oil levels one day after treatments were applied (hatched bar in Figure 7) followed no particular pattern. Several of the treatments increased slightly while the treatments tillage-fertilizer-irrigation (Treatment 6), tillage-fertilizer-plastic sheeting-irrigation-straw mulch (Treatment 7), and supertillage-fertilizer-plastic sheeting-irrigation-peat mulch-inoculum (Treatment 10) decreased considerably. Average oil content for the tilled treatments decreased by 0.15 percent oil, a 36% reduction. The wide variations in oil content recorded at this depth are probably a function of two factors. The tilling and chiseling of the soil probably mixed the oil in this interval to some

extent. The limit of the extraction method to measure the low levels of oil encountered at this depth is another factor.

Average values for oil content increased 4% in the 205 day soil samples above the previous sampling. Both increases and decreases were measured but most of these changes were on the order of 0.1 percent oil (Table 9), a value easily attributable to error in the extraction method. The 315 day samples exhibited a similar relationship by decreasing an average of 2.1% from the previous sampling. Changes in soil oil content were on the order of 0.1 percent oil (Table 9). Treatment 3 (tillage-fertilizer) showed a substantial increase in oil content which was entirely attributable to an increase in one of the replications. The reason for this increase is not known. None of the changes in oil content were significantly different than the control in either the 205 or 315 day samplings.

Comparison Contrasts of Soil Amendments

Comparison contrasts place treatments sharing a common amendment into one group. Contrasts were utilized to test the effectiveness of an amendment in reducing soil oil content. Nine contrasts were made on differences in oil content between the 315 and one day samplings at each depth. Contrasts included tillage versus non-tillage, irrigated versus non-irrigated, fertilized versus non-fertilized, plastic covered versus non-plastic covered, mulch versus non-mulch, the combination of tillage-fertilizer-irrigation versus the remaining treatments, calcium chloride versus the remaining treatments, peat mulch versus straw mulch, and super tillage versus the remaining treatments. Of these twenty-seven contrasts, only one had significantly lower oil levels,

tillage versus non-tillage in the 0 to 5 cm interval. Two other contrasts approached significance. Irrigated treatments showed less change in soil oil content than non-irrigated treatments at the 20% significance level in the 0 to 5 cm depth. Plastic covered treatments had significantly lower oil levels than non-plastic covered treatments at the 15% significance level in the 15 to 46 cm depth interval.

Fertility

Nitrate-N, phosphorous, and potassium were measured in soil samples before treatments were applied. Nitrate-N was measured again in the 315 day samples. Average nitrate-N for the three depth increments are shown in Table 10. A comparison contrast showed fertilized plots had significantly higher nitrate-N levels than non-fertilized plots at all three depths ($P=0.05$).

Table 10. Average soil nitrate-nitrogen before and after fertilization.

Depth (cm)	Average Soil Nitrate-Nitrogen (ppm)		
	Pretreatment	Unfertilized*	Fertilized*
0-5	6	4	178
5-15	3	2	25
15-46	6	4	18

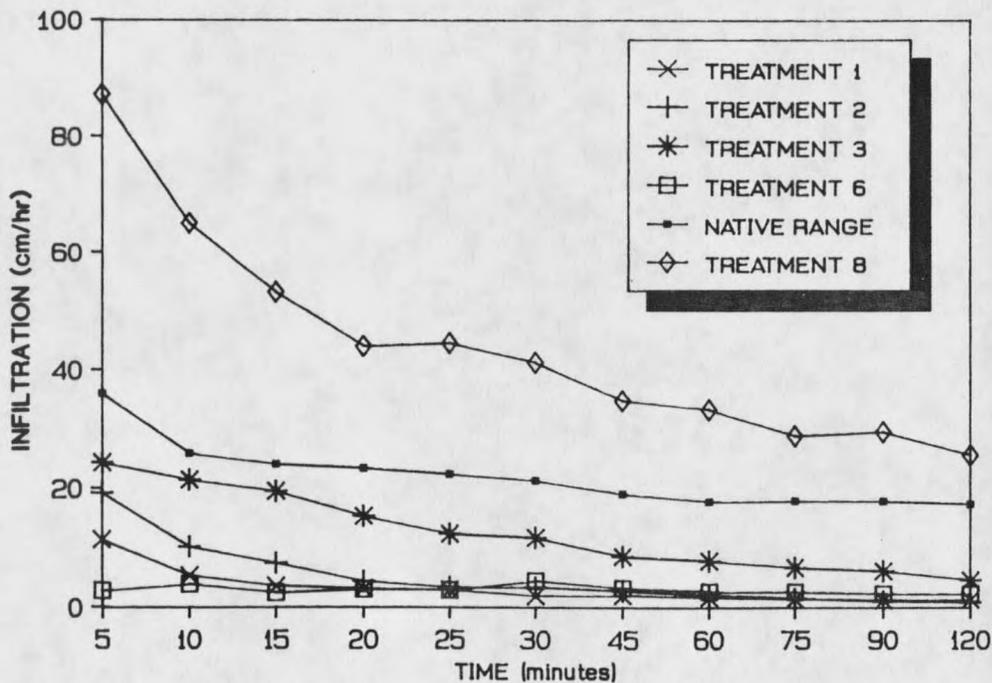
* Unfertilized and fertilized values measured in samples collected 315 days after treatment.

Phosphorous averaged 13, 18, and 13 ppm for the 0 to 5, 5 to 15, and 15 to 46 cm intervals, respectively. Values ranged from a maximum of 26 to a minimum of 6 ppm. Potassium averaged 530, 414, and 514 ppm for the three respective depths. The maximum recorded was 668 and the minimum was 316 ppm. An ANOVA showed that there was no significant

difference between treatments for either phosphorus or potassium content ($P=0.05$).

Infiltration

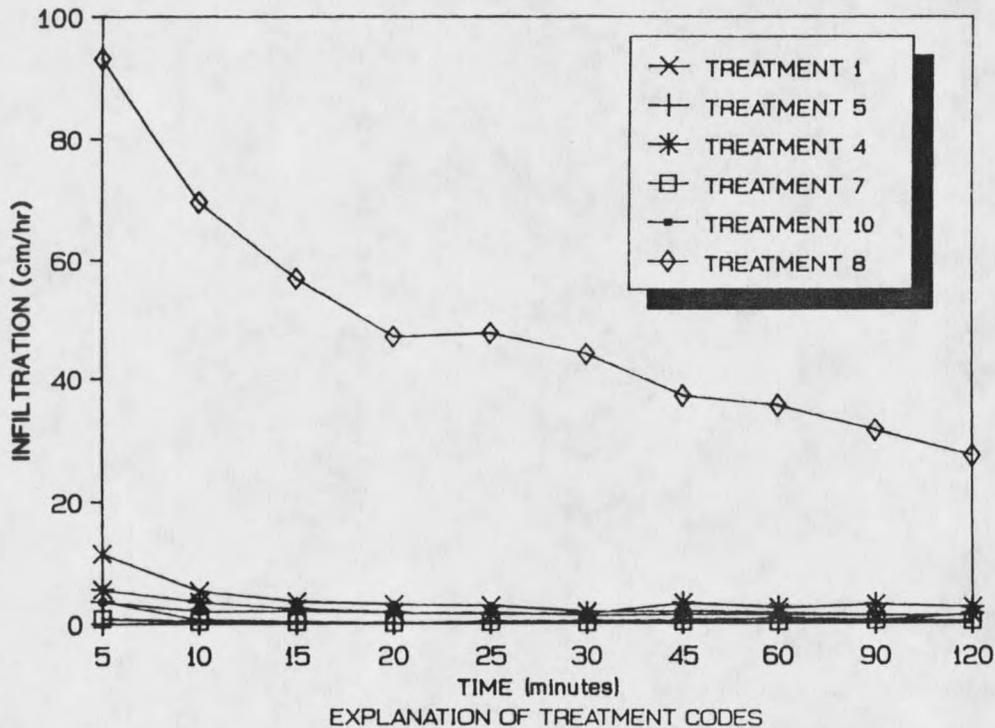
Results of the infiltration tests are illustrated in Figures 8 and 9. Statistical comparisons were made on the infiltration rate reached at the end of the 120 minute period. Treatment 8 (tillage-fertilizer- CaCl_2) had significantly higher infiltration ($P=0.05$) than native range and all other treatments. Native range had significantly higher infiltration than the remaining treatments. According to the Soil



EXPLANATION OF TREATMENT CODES

- | | |
|---|-------------------------------------|
| 1. Control | 4. Tillage; Clear plastic sheeting. |
| 2. Tillage | 5. Tillage; Irrigation. |
| 3. Tillage; Fertilizer. | 6. Tillage; Fertilizer; Irrigation. |
| 7. Tillage; Fertilizer; Clear plastic sheeting; Irrigation; Straw mulch. | |
| 8. Tillage; Fertilizer; Calcium chloride. | |
| 9. Supertillage; Fertilizer; Clear plastic sheeting; Irrigation; Peat mulch. | |
| 10. Supertillage; Fertilizer; Clear plastic sheeting; Irrigation; Peat mulch; Inoculum. | |

Figure 8. Infiltration rates of selected treatments.



- EXPLANATION OF TREATMENT CODES
- | | |
|---|-------------------------------------|
| 1. Control | 4. Tillage; Clear plastic sheeting. |
| 2. Tillage | 5. Tillage; Irrigation. |
| 3. Tillage; Fertilizer. | 6. Tillage; Fertilizer; Irrigation. |
| 7. Tillage; Fertilizer; Clear plastic sheeting; Irrigation; Straw mulch. | |
| 8. Tillage; Fertilizer; Calcium chloride. | |
| 9. Supertillage; Fertilizer; Clear plastic sheeting; Irrigation; Peat mulch. | |
| 10. Supertillage; Fertilizer; Clear plastic sheeting; Irrigation; Peat mulch; Inoculum. | |

Figure 9. Infiltration rates of selected treatments.

Conservation Service (1951), infiltration on native range would be classified as rapid, Treatment 8 very rapid, and the other treatments very slow to slow. The increase in infiltration on the calcium chloride treatment is attributed to the exchange of calcium for sodium on the cation exchange sites. By replacing calcium with sodium, clay particles are reoriented from a dispersed condition to a flocculated arrangement. Flocculated soils allow the transmission of water through a soil much more readily than a dispersed soil.

Several comparison contrasts were significant at the 5% level. Tilled treatments had significantly higher infiltration than the non-

tilled treatment (control). Those treatments that included fertilizer also had significantly higher infiltration rates than those treatments which were not fertilized. Conversely, those treatments which were irrigated had significantly lower infiltration than non-irrigated treatments. Irrigation most likely caused dispersion of the soil accounting for the reduction in infiltration. Plastic covered plots and plots mulched with either straw or peat also had significantly lower infiltration rates. Three of the four plastic covered treatments and the mulch treatments were also irrigated, accounting for this result.

Temperature

Soil temperatures were higher than the control under the plastic covered plots at all depths on the majority of the days when temperatures were measured. Results of temperature measurements are shown in Table 11. Probes buried 2 cm in the soil registered temperatures 1 to 9°C higher than the control plot. Increases in soil temperature at 10 cm varied from 1 to 5.3°C higher than non-plastic covered plots. Soil temperatures at 25 cm varied from 4°C lower on plastic covered plots to 5°C higher. The -4°C difference between plastic and non-plastic covered plots measured on March 21 was probably due to instrument error. Probes at 50 cm measured temperature differences ranging from -2.5°C lower on plastic covered plots to 4°C higher.

Table 11. Soil temperature on plastic covered and non-covered plots.

Date	PROBE DEPTH 2 cm				PROBE DEPTH 10 cm			
	Mean Temperature (°C)		Difference (°C)	P-Value	Mean Temperature (°C)		Difference (°C)	P-Value
	Plastic	Control			Plastic	Control		
9/8/87	34.7	26.3	8.4	.014+	20.3	17.3	3.0	.017+
9/10/87	40.7	32.7	8.0	.031+	23.0	20.7	2.3	.010+
9/21/87	39.0	33.7	5.3	.104	21.5	20.0	1.5	.025+
10/8/87	13.0	9.7	3.3	.054	13.5	10.0	3.5	.045+
10/20/87	17.3	12.7	4.6	.111	9.0	6.0	3.0	.000+
11/13/87	8.3	6.7	1.6	.065	6.0	5.0	1.0	.003+
12/28/87	-3.7	-6.0	2.3	.096	-3.7	-7.3	3.6	.047+
2/1/88	-4.0	-9.0	5.0	.006+	-7.0	-10.0	3.0	.102
3/3/88	6.3	5.0	1.3	*	3.0	2.0	1.0	*
3/21/88	9.0	0.0	9.0	.108	9.0	3.7	5.3	*
4/15/88	28.0	20.3	7.7	.140	13.0	8.0	5.0	*
4/29/88	17.0	15.5	1.5	.102	13.6	11.7	2.9	.005+
5/13/88	29.0	26.3	2.7	.206	23.3	22.0	1.3	*
5/24/88	27.6	20.7	6.9	.088	25.3	21.3	4.0	.078
6/9/88	22.5	15.0	7.5	*	18.0	13.0	5.0	*
6/23/88	27.0	26.0	1.0	*	25.0	22.0	3.0	*
7/15/88	38.7	31.7	7.0	.007+	29.0	23.7	5.3	.013+

Date	PROBE DEPTH 25 cm				PROBE DEPTH 50 cm			
	Mean Temperature (°C)		Difference (°C)	P-Value	Mean Temperature (°C)		Difference (°C)	P-Value
	Plastic	Control			Plastic	Control		
9/8/87	18.7	15.7	3.0	.000+	17.7	16.7	1.0	.003+
9/10/87	16.7	17.0	-0.3	.899	18.0	16.7	1.3	.103
9/21/87	18.0	16.0	2.0	.001+	17.0	15.7	1.3	.103
10/8/87	13.3	11.0	2.3	.010+	14.0	12.7	1.3	.102
10/20/87	7.7	5.0	2.7	.007+	9.0	8.0	1.0	.006+
11/13/87	3.7	2.7	1.0	.003+	3.5	6.0	-2.5	.500
12/28/87	-3.3	-4.3	1.0	.112	-2.0	-3.7	1.7	.222
2/1/88	-6.0	-11.0	5.0	.069	-4.0	-3.3	0.7	.317
3/3/88	0.0	0.0	0.0	*	1.0	1.0	0.0	*
3/21/88	-0.7	3.7	-4.0	.306	1.8	2.3	-0.5	.874
4/15/88	11.0	7.7	3.3	.074	7.8	5.3	2.5	.063
4/29/88	13.0	10.7	2.3	.124	11.6	9.6	2.0	.004+
5/13/88	18.7	15.7	3.0	.273	15.7	15.3	0.4	.403
5/24/88	22.3	19.3	3.0	.102	19.3	17.3	2.0	.147
6/9/88	19.0	15.0	4.0	*	20.0	17.5	2.5	*
6/23/88	22.0	18.0	4.0	*	20.0	16.0	4.0	*
7/15/88	24.3	19.3	5.0	.000+	22.6	19.6	3.0	.005+

* Indicates 2 or more thermocouples were not working.

+ Indicates value is significant at 0.05.

SUMMARY AND CONCLUSIONS

Ten treatments were evaluated at the Shay-Wait study area to test soil amendments which might improve the rate of oil degradation on contaminated soils. Amendments including tillage, fertilizer, irrigation, mulch, plastic sheeting, inoculum, and calcium chloride were used in a variety of combinations to make up the treatments. All the amendments were readily available from local sources and were applied with normal farm equipment. Soils were sampled four times during the study: before treatment application, and then one day, 205 days, and 315 days after treatments were applied.

Changes in soil oil content were monitored through time and used to measure oil degradation rate. The treatment tillage-fertilizer-calcium chloride (Treatment 8) had a significantly higher degradation rate than the control in the 205 day period, but, by the end of 315 days, oil content had risen slightly and was no longer significantly lower than the control. Overall, this calcium chloride treatment exhibited the largest decrease in soil oil content (22%) over the course of the study. Infiltration on this treatment was significantly higher than non-contaminated soil, and was significantly higher than any of the other treatments. The factor responsible for both the decrease in oil content and the higher infiltration rate was the exchange of calcium with sodium on the cation exchange sites of colloidal particles. This caused flocculation of the dispersed soil, providing a better flux of air and water into the soil.

Tillage was shown to significantly reduce soil oil content in the 0 to 5 cm depth interval, a result of the mixing of soil to a depth of 15-20 cm. A comparison contrast of the change in oil content between the 315 day sampling and the one day sampling for tillage versus non-tillage showed tilled treatments to have significantly lower oil levels. Tilled plots also had significantly higher infiltration than non-tilled plots, another indication that aeration and water flux is an important factor in oil degradation.

A comparison contrast indicated irrigated treatments had significantly lower degradation rates and lower infiltration than non-irrigated treatments. Irrigation probably dispersed the sodic soils, restricting the movement of the necessary air and water into the profile needed for oil degradation.

None of the other amendments -- fertilizer, clear plastic sheeting, mulch, inoculum, or supertillage -- were found to improve oil degradation. Clear plastic sheeting increased soil temperatures at all depths measured but this increase did not significantly influence the rate of degradation on plots covered with plastic sheeting.

Over the term of the study, no single treatment had significantly higher degradation rates than the control. Two factors were primarily responsible for this result. The distribution of oil content on the Shay-Wait site was extremely variable. This limited the precision of the experimental design, making it harder to detect actual treatment effects from changes due to random variation. Secondly, treatments were monitored for a relatively short period of time. In the cold and

dry environment of the Northern Great Plains, even enhanced degradation of oil probably occurs at a slow rate.

LITERATURE CITED

- Adriano, D.C. 1986. Trace Elements in the Terrestrial Environment. Springer-Verlag, New York. 533 p.
- Arrigo, J. personal communication, January 27, 1988. Montana State Department of Health and Environmental Sciences, Water Quality Bureau.
- Atlas, R.M. 1981. Microbial degradation of petroleum hydrocarbons: An environmental perspective. Microbiological Review. 45:180-209.
- Atlas, R.M. 1977. Stimulated petroleum biodegradation. Critical Reviews in Microbiology. 5:371-386.
- Baker, J.M. 1970. The effect of oils on plants. Environmental Pollution. 1:27-44.
- Bartha, R. 1986. Biotechnology of petroleum pollutant biodegradation. Microbiological Ecology. 12:155-172.
- Black, C.A. ed. 1965. Standard Methods of Soil Analysis. American Society of Agronomy Monograph No. 9, Parts 1 and 2. Madison, Wisconsin.
- Bremner, A. 1965. Inorganic forms of nitrogen. *in* C.A. Black, ed. Methods of Soil Analysis. American Society of Agronomy Monograph No. 9, Part 2. Madison, Wisconsin. pp. 1179-1237.
- Brown, K.W., K.C. Donnelly, J.C. Thomas, and L.E. Deuel, Jr. 1981. Factors influencing the biodegradation of API separator sludges applied to soils, *in* Land Disposal: Hazardous Waste, Proceedings of the 7th Annual Research Symposium at Philadelphia, PA. D. W. Schultz, ed. US EPA. Cincinnati, OH. EPA 600/9-81-002b. p. 188-199.
- Cansfield, P.E. and G.J. Racz. 1978. Degradation of hydrocarbon sludges in the soil. Canadian Journal of Soil Science. 58:339-45. ✓
- Carmer, S.G., and W.M. Walker. 1985. Pairwise multiple comparisons of treatment means in agronomic research. Journal of Agronomic Education. 14:19-26.
- Carr, R.H. 1919. Vegetative growth in soils containing crude petroleum. Soil Science. 8:67-68.
- Colwell, R.R., A.L. Mills, J.D. Walker, P. Garcia-Tello, and V. Campos. 1978. Microbial ecology studies of the Metula spill in the Straits of Magellan. Journal of the Fisheries Research Board of Canada. 35:573-580.
- Currier, H.B. 1951. Herbicidal properties of benzene and certain methyl derivatives. Hilgardia. 20:383-406.

- de Jong, E. 1980a. Reclamation problems and procedures for the oil industry on the Canadian prairies. *Reclamation Review*. 3:75-85.
- de Jong, E. 1980b. The effect of a crude oil spill on cereals. *Environmental Pollution (Series A)*. 22:187-196.
- Dibble, J.T., and R. Bartha. 1979a. Rehabilitation of oil-inundated agricultural land: A case history. *Soil Science*. 128:56-60.
- Dibble, J.T., and R. Bartha. 1979b. Leaching aspects of oil sludge biodegradation in soil. *Soil Science*. 127:000-000. ✓
- Dibble, J.T., and R. Bartha. 1979c. Effect of environmental parameters on the biodegradation of oil sludge. *Applied Environmental Microbiology*. 37:729-739. ✓
- Donahue, R.L., R.W. Miller, and J.C. Shickluna. 1983. *Soils: an Introduction to Soils and Plant Growth*. Fifth ed. Prentice-Hall, Inc., Englewood Cliffs, NJ. p. 145.
- Dotson, G.K., R.B. Dean, W.B. Cooke, and B.A. Kennar. 1970. Land spreading, a conserving and non-polluting method of disposing of oily wastes, *in* *Advances in Water Pollution*, 5th International Water Pollution Research Conference. Vol. 1, Section 2. Pergamon Press, N.Y. 36/1-16.
- Ellis, R., Jr. and R.S. Adams, Jr. 1961. Contamination of soils by petroleum hydrocarbons. *Advances in Agronomy*. 13:197-216. ✓
- EPA. 1987. Assessment of toxicity of arsenic, cadmium, lead, and zinc in soil, plants, and livestock in the Helena Valley of Montana. U.S. Environmental Protection Agency. Contract No. 68-01-7251. Denver, Colorado. 206 p.
- Follett, R.H. and W.C. Lindsay. 1971. Changes in DTPA-extractable zinc, iron, manganese, and copper in soils following fertilization. *Soil Science Society of America Proceedings*. 35:600-02.
- Francke, H.C. and F.E. Clark. 1974. *Disposal of Oily Wastes by Microbial Assimilation*. Union Carbide. Oak Ridge, Tennessee. Prepared for the US Atomic Energy Commission. Contract No. W7504 eng 26. Y1934. 44 p.
- Franson, M.A., M.C. Rand, A.E. Greenberg, and M.J. Taras. 1976. *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association. Washington, D.C.

- Gudin, C., and W.J. Syrratt. 1975. Biological aspects of land rehabilitation following hydrocarbon contamination. *Environmental Pollution*. 8:107-112.
- Haise H.R., W.W. Donnan, J.T. Phelan, L.F. Lawhon, and D.G. Shockley. 1956. The use of cylinder infiltrometers to determine the intake characteristics of irrigated soils. USDA Agricultural Research Service and Soil Conservation Service publication ARS 41-7. U.S. Government Printing Office, Washington, D.C. 10p.
- Huddleston, R.L. 1979. Solid-waste disposal: Landfarming. *Chemical Engineering*. 86:119-124.
- Jobson, A., M. McLaughlin, F. Cook, and D.W.S. Westlake. 1974. Effect of amendments on the microbial utilization of oil applied to soil. *Applied Microbiology*. 27:166-171.
- Jobson, A., F.D. Cook, and D.W.S. Westlake. 1972. Microbial utilization of crude oil. *Applied Microbiology*. 23:1082-1089.
- Johnson, A.I. 1963. A field method for measurement of infiltration. Geological Survey Water-Supply Paper 1544-F. U.S. Government Printing Office. Washington, D.C. 27 p.
- Kincannon, C. 1972. Oily Waste Disposal by Soil Cultivation Process. US EPA. Environmental Protection Technology Series. Washington, D.C. Office of Research and Monitoring. EPA-R2-72-110. 115 p.
- Knickman, E. 1960. *Umschau*. 60:118-119.
- Loynachan, T.E. 1978. Low-temperature mineralization of crude oil in soil. *Journal of Environmental Quality*. 7:494-500. ✓
- McGill, W.B. 1977. Soil restoration following oil spills - a review. *The Journal of Canadian Petroleum Technology*. 16:60-67.
- Mitchell, W.W., T.E. Loynachan, and J.D. McKendrick. 1979. Effects of tillage and fertilization on persistence of crude oil contamination in an Alaskan soil. *Journal of Environmental Quality*. 8:525-532.
- Murphy, H.F. 1929. Some effects of crude petroleum on nitrate production, seed germination, and growth. *Soil Science*. 27:117-120.
- Olsen, S.R. and L.A. Dean. 1965. Phosphorus. *in* C.A. Black, ed. *Methods of Soil Analysis*. American Society of Agronomy Monograph No. 9, Part 2. Madison, Wisconsin. pp. 1035-1049.
- Plice, M.J. 1948. Some effects of crude petroleum on soil fertility. *Soil Science Society of America Proceedings*. 13:413-416.

- Pratt, R.F. 1965. Potassium. in C.A. Black, ed. Methods of Soil Analysis. Amer. Soc. of Agronomy Monograph No. 9, Part 2. Madison, Wisconsin. pp. 1022-1030.
- Raymond, L., J.O. Hudson, and V.W. Jamison. 1976. Oil degradation in soil. Applied and Environmental Microbiology. 31:522-535. ✓
- Richards, L.A., ed. 1954. Diagnosis and improvement of saline and alkali soil. Agricultural Handbook No. 60. U.S. Department of Agriculture, Washington, D.C. 160 pp.
- Rowell, M.J. 1977. The effect of crude oil spills on soils - a review of literature, in J. A. Toogood, ed. The Reclamation of Agricultural Soils After Oil Spills, Part 1, Research. Alberta Institute of Pedology, Publication No. M-77-11. University of Alberta, Edmonton, Canada. 139 pp. ✓
- SCS. 1951. Soil Conservation Service Staff. Soil Survey Manual. U.S. Department of Agriculture Agricultural Handbook No. 18. Washington, D.C. 503 p.
- Sandvik, S., A. Lode, and T.A. Pedersen. 1986. Biodegradation of oily sludge in Norwegian soils. Applied Microbiology and Biotechnology. 23:297-301.
- Schwendinger, R.B. 1968. Reclamation of soil contaminated with oil. Journal of the Institute of Petroleum. 54:182-197.
- Sims, J.R. and G.D. Jackson. 1971. Rapid analysis of soil nitrate with chromotropic acid. Soil Science Society of America Proceedings 35:603-06.
- Skujins, J., and S.O. McDonald. 1985. Waste oil biodegradation and changes in microbial populations in a semiarid soil, in Planetary Ecology. D. Caldwell, J. Brierley, and C. Brierley, eds. Van Nostrand Reinhold Co., New York.
- Skujins, J., S.O. McDonald, and W.G. Knight. 1983. Metal ion availability during biodegradation of waste oil in semi-arid soils. Environmental Biochemistry Ecological Bulletin. 35:341-350.
- State of Montana Oil and Gas Conservation Commission, July 12, 1988. Shelby, Montana field office records.
- Stone, R.W., M.R. Fenske, and A.G.C. White. 1942. Bacteria attacking petroleum and oil fractions. Journal of Bacteriology. 44:169-178.
- Tonnsen, J.J. ed. 1985. Montana Oil and Gas Fields Symposium, Vol. 1. Montana Geological Society, Billings, Montana.

- Toogood, J.A. 1977. Effects of oil spills on physical properties of soils, in J.A. Toogood, ed. The Reclamation of Agricultural Soils After Oil Spills, Part 1, Research. Alberta Institute of Pedology, Publication No. M-77-11. University of Alberta, Edmonton, Canada. 139 pp.
- Udo, E.J. and A.A. Fayemi. 1975. The effect of oil pollution of soil on germination, growth, and nutrient uptake of corn. Journal of Environmental Quality. 4:537-540.

APPENDIX

Analysis of Variance Tables

Table 12. Analysis of variance and treatment means for pretreatment soil oil content in the 0 to 5 cm depth interval.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	29.12	14.56		
Treatments	9	37.25	4.13	0.89	.5510
Error	18	83.54	4.64		

Treatment Means			
Treatment	Mean	Treatment	Mean
1	4.00	6	7.14
2	3.31	7	5.27
3	5.46	8	6.81
4	5.18	9	4.57
5	4.59	10	5.70

Table 13. Analysis of variance and treatment means for the difference in soil oil content between tilled treatments and the control in the 0 to 5 cm depth interval.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	1.27	0.63		
Treatments	1	31.22	31.22	7.90	.0092
Error	26	102.69	3.94		

Treatment Means			
Treatment	Mean	Treatment	Mean
Tilled	-3.40	Non-tilled	0.00

Table 14. Analysis of variance, treatment means, and least significant difference sets for the difference in soil oil content between the 205 and one day soil samples in the 0 to 5 cm depth interval.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	0.74	0.37		
Treatments	9	4.50	0.50	2.76	.0320
Error	18	3.26	0.18		

Treatment Means and Least Significant Difference Sets					
Treatment	Mean	LSD	Treatment	Mean	LSD
1	0.28	cb	6	0.86	c
2	-0.07	ab	7	0.33	cb
3	-0.20	ab	8	-0.73	a
4	-0.08	ab	9	0.00	b
5	-0.08	ab	10	-0.04	ab

Table 15. Analysis of variance, treatment means, and contrast coefficients for the difference in soil oil content between the 315 and one day soil samples in the 0 to 5 cm depth interval.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	0.96	0.49		
Treatments	9	7.76	0.86	2.16	.0791
Error	18	7.20	0.40		

Treatment Means			
Treatment	Mean	Treatment	Mean
1	1.28	6	0.53
2	0.03	7	-0.21
3	-0.35	8	-0.53
4	-0.42	9	-0.23
5	0.03	10	-0.08

Contrast Coefficients			
Contrast	Coefficients	t	P
Fertilize/non-fertilize	0,-6,3,-6,-6,3,3,3,3,3	-0.08	.934
Till/non-till	-9,1,1,1,1,1,1,1,1,1	-3.67	.002
Irrigate/non-irrigate	0,-5,-5,-5,4,4,4,-5,4,4	1.33	.201
Plastic covered/non-covered	0,-4,-4,5,-4,-4,5,-4,5,5	-0.72	.479
Till-fertilize-irrigate/others	0,-4,-4,-4,-4,5,5,-4,5,5	1.02	.320
Calcium chloride/others	0,-1,-1,-1,-1,-1,-1,8,-1,-1	-1.13	.272
Mulch/non-mulch	0,-3,-3,-3,-3,-3,6,-3,6,6	-0.20	.839
Peat mulch/straw mulch	0,0,0,0,0,0,-2,0,1,1	0.13	.892
Supertillage/others	0,-2,-2,-2,-2,-2,-2,-2,7,7	-0.07	.948

Table 16. Analysis of variance and treatment means for pretreatment soil oil content in the 5 to 15 cm depth interval.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	15.58	7.79		
Treatments	9	30.65	3.40	1.55	.2057
Error	18	39.62	2.20		

Treatment Means			
Treatment	Mean	Treatment	Mean
1	0.68	6	1.29
2	0.84	7	0.94
3	3.77	8	0.44
4	1.86	9	0.72
5	0.83	10	2.67

Table 17. Analysis of variance and treatment means for the difference in soil oil content between tilled treatments and the control in the 5 to 15 cm depth interval.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	5.32	2.66		
Treatments	1	0.50	0.50	0.15	.7077
Error	26	91.43	3.51		

Treatment Means			
Treatment	Mean	Treatment	Mean
Tilled	0.43	Non-tilled	0.00

Table 18. Analysis of variance and treatment means for the difference in soil oil content between the 205 and one day soil samples in the 5 to 15 cm depth interval.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	0.49	0.24		
Treatments	9	2.02	0.22	0.31	.9609
Error	18	13.00	0.72		

Treatment Means			
Treatment	Mean	Treatment	Mean
1	-0.32	6	-0.40
2	0.18	7	-0.22
3	0.00	8	-0.21
4	0.17	9	-0.08
5	-0.21	10	-0.73

Table 19. Analysis of variance, treatment means, and contrast coefficients for the difference in soil oil content between the 315 and one day soil samples in the 5 to 15 cm depth interval.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	1.08	0.54		
Treatments	9	4.31	0.47	0.73	.6739
Error	18	11.75	0.65		

Treatment Means			
Treatment	Mean	Treatment	Mean
1	-0.20	6	-0.93
2	-0.37	7	-0.86
3	-0.34	8	-0.92
4	-1.13	9	0.10
5	-0.37	10	-0.84

Contrast Coefficients			
Contrast	Coefficients	t	P
Fertilize/non-fertilize	0, -6, 3, -6, -6, 3, 3, 3, 3, 3	-0.04	.972
Till/non-till	-9, 1, 1, 1, 1, 1, 1, 1, 1, 1	-0.88	.392
Irrigate/non-irrigate	0, -5, -5, -5, 4, 4, 4, -5, 4, 4	0.35	.728
Plastic covered/non-covered	0, -4, -4, 5, -4, -4, 5, -4, 5, 5	-0.31	.764
Till-fertilize-irrigate/others	0, -4, -4, -4, -4, 5, 5, -4, 5, 5	-0.02	.982
Calcium chloride/others	0, -1, -1, -1, -1, -1, -1, 8, -1, -1	-0.66	.515
Mulch/non-mulch	0, -3, -3, -3, -3, -3, 6, -3, 6, 6	0.43	.669
Peat mulch/straw mulch	0, 0, 0, 0, 0, 0, -2, 0, 1, 1	0.86	.401
Supertillage/others	0, -2, -2, -2, -2, -2, -2, -2, 7, 7	0.89	.384

Table 20. Analysis of variance and treatment means for pretreatment soil oil content in the 15 to 46 cm depth interval.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	0.72	0.36		
Treatments	9	2.45	0.27	1.24	.3320
Error	18	3.96	0.22		

Treatment Means			
Treatment	Mean	Treatment	Mean
1	0.21	6	0.56
2	0.08	7	0.50
3	1.01	8	0.11
4	0.46	9	0.20
5	0.25	10	0.74

Table 21. Analysis of variance and treatment means for the difference in soil oil content between tilled treatments and the control in the 15 to 46 cm depth interval.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	0.07	0.03		
Treatments	1	0.05	0.05	0.78	.3844
Error	26	1.94	0.07		

Treatment Means			
Treatment	Mean	Treatment	Mean
Tilled	-0.15	Non-tilled	0.00

Table 22. Analysis of variance and treatment means for the difference in soil oil content between the 205 and one day soil samples in the 15 to 46 cm depth interval.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	0.03	0.01		
Treatments	9	0.11	0.01	0.52	.8385
Error	18	0.45	0.02		

Treatment Means			
Treatment	Mean	Treatment	Mean
1	-0.11	6	0.07
2	-0.06	7	0.04
3	0.10	8	0.04
4	0.01	9	0.06
5	-0.05	10	0.02

Table 23. Analysis of variance, treatment means, and contrast coefficients for the difference in soil oil content between the 315 and one day soil samples in the 15 to 46 cm depth interval.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	0.21	0.10		
Treatments	9	1.03	0.11	1.07	.4313
Error	18	1.94	0.10		

Treatment Means			
Treatment	Mean	Treatment	Mean
1	-0.11	6	0.08
2	0.01	7	-0.07
3	0.53	8	-0.06
4	-0.06	9	-0.02
5	-0.02	10	-0.17

Contrast Coefficients			
Contrast	Coefficients	t	P
Fertilize/non-fertilize	0, -6, 3, -6, -6, 3, 3, 3, 3, 3	0.54	.597
Till/non-till	-9, 1, 1, 1, 1, 1, 1, 1, 1, 1	0.70	.495
Irrigate/non-irrigate	0, -5, -5, -5, 4, 4, 4, -5, 4, 4	-1.14	.268
Plastic covered/non-covered	0, -4, -4, 5, -4, -4, 5, -4, 5, 5	-1.50	.151
Till-fertilize-irrigate/others	0, -4, -4, -4, -4, 5, 5, -4, 5, 5	-0.99	.334
Calcium chloride/others	0, -1, -1, -1, -1, -1, -1, 8, -1, -1	-0.46	.649
Mulch/non-mulch	0, -3, -3, -3, -3, -3, 6, -3, 6, 6	-1.26	.224
Peat mulch/straw mulch	0, 0, 0, 0, 0, 0, -2, 0, 1, 1	-0.09	.932
Supertillage/others	0, -2, -2, -2, -2, -2, -2, -2, 7, 7	-1.00	.326

Table 24. Analysis of variance and treatment means for pretreatment nitrate-nitrogen content in the 0 to 5 cm depth interval.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	420.49	210.24		
Treatments	9	278.23	30.915	0.80	.6198
Error	18	693.72	38.540		

Treatment Means			
Treatment	Mean	Treatment	Mean
1	7.40	6	2.63
2	11.60	7	6.66
3	7.00	8	1.50
4	5.66	9	8.66
5	6.83	10	1.70

Table 25. Analysis of variance, treatment means and contrast coefficients of nitrate-nitrogen content in the 0 to 5 cm depth interval in the 315 day samples.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	27163	13582		
Treatments	9	4.49x10 ⁵	49992	4.97	.0019
Error	18	1.81x10 ⁵	10066		

Treatment Means			
Treatment	Mean	Treatment	Mean
1	3.16	6	217.50
2	8.60	7	130.06
3	165.00	8	33.70
4	0.50	9	400.10
5	4.06	10	120.20

Contrast Coefficients				
Contrast	Coefficients		t	P
Fertilize/non-fertilize	-6, -6, 4, -6, -6, 4, 4, 4, 4, 4		4.67	.000

Table 26. Analysis of variance and treatment means for pretreatment phosphorus content in the 0 to 5 cm depth interval.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	31.23	15.61		
Treatments	9	124.61	13.84	0.54	.8278
Error	18	462.77	25.71		

Treatment Means			
Treatment	Mean	Treatment	Mean
1	13.60	6	12.00
2	17.67	7	10.40
3	14.23	8	12.57
4	15.50	9	11.47
5	14.63	10	12.27

Table 27. Analysis of variance and treatment means for pretreatment potassium content in the 0 to 5 cm depth interval.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	944	472.13		
Treatments	9	38492	4276.90	0.84	.5888
Error	18	91438	5079.90		

Treatment Means			
Treatment	Mean	Treatment	Mean
1	536.0	6	511.3
2	494.7	7	532.0
3	542.0	8	464.0
4	610.7	9	538.3
5	533.3	10	540.3

Table 28. Analysis of variance and treatment means for pretreatment nitrate-nitrogen content in the 5 to 15 cm depth interval.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	31.02	15.51		
Treatments	9	31.15	3.46	1.20	.3527
Error	18	51.91	2.88		

Treatment Means			
Treatment	Mean	Treatment	Mean
1	3.46	6	2.16
2	4.93	7	2.36
3	3.23	7	1.96
4	3.80	9	2.43
5	1.63	10	1.60

Table 29. Analysis of variance, treatment means and contrast coefficients of nitrate-nitrogen content in the 5 to 15 cm depth interval in the 315 day samples.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	1399.5	699.75		
Treatments	9	5882.6	653.62	2.48	.0479
Error	18	4735.1	263.06		

Treatment Means			
Treatment	Mean	Treatment	Mean
1	2.33	6	32.97
2	4.30	7	8.63
3	40.80	8	15.83
4	0.16	9	29.80
5	0.76	10	19.10

Contrast Coefficients				
Contrast	Coefficients		t	P
Fertilize/non-fertilize	-6, -6, 4, -6, -6, 4, 4, 4, 4, 4		3.74	.001

Table 30. Analysis of variance and treatment means for pretreatment phosphorus content in the 5 to 15 cm depth interval.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	186.75	93.37		
Treatments	9	135.90	15.10	1.25	.3257
Error	18	217.00	12.05		

Treatment Means			
Treatment	Mean	Treatment	Mean
1	19.33	6	14.63
2	19.00	7	18.57
3	17.57	8	20.20
4	13.67	9	18.47
5	19.43	10	15.53

Table 31. Analysis of variance and treatment means for pretreatment potassium content in the 5 to 15 cm depth interval.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	10356	5178.10		
Treatments	9	7567	840.82	0.62	.7665
Error	18	24472	1359.50		

Treatment Means			
Treatment	Mean	Treatment	Mean
1	405.7	6	410.3
2	412.7	7	403.7
3	421.0	8	415.0
4	399.7	9	453.0
5	392.7	10	424.0

Table 32. Analysis of variance and treatment means for pretreatment nitrate-nitrogen content in the 15 to 46 cm depth interval.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	113.40	56.70		
Treatments	9	338.94	37.66	0.76	.6536
Error	18	892.59	49.58		

Treatment Means			
Treatment	Mean	Treatment	Mean
1	3.86	6	4.16
2	9.83	7	2.33
3	4.66	8	7.13
4	5.43	9	5.06
5	2.16	10	13.60

Table 33. Analysis of variance, treatment means and contrast coefficients of nitrate-nitrogen content in the 15 to 46 cm depth interval in the 315 day samples.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	327.38	163.69		
Treatments	9	2342.10	260.24	2.83	.0288
Error	18	1654.20	91.90		

Treatment Means			
Treatment	Mean	Treatment	Mean
1	2.73	6	26.33
2	5.20	7	5.53
3	16.27	8	18.53
4	4.43	9	23.67
5	2.60	10	19.83

Contrast Coefficients				
Contrast	Coefficients		t	P
Fertilize/non-fertilize	-6, -6, 4, -6, -6, 4, 4, 4, 4, 4		4.09	.000

Table 34. Analysis of variance and treatment means for pretreatment phosphorus content in the 15 to 46 cm depth interval.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	34.76	17.38		
Treatments	9	36.70	4.07	0.79	.6263
Error	18	92.49	5.13		

Treatment Means			
Treatment	Mean	Treatment	Mean
1	11.40	6	12.43
2	11.73	7	12.07
3	15.10	8	13.47
4	11.60	9	11.40
5	13.17	10	12.80

Table 35. Analysis of variance and treatment means for pretreatment potassium content in the 15 to 46 cm depth interval.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	3080	1540.3		
Treatments	9	29783	3309.2	2.57	.0420
Error	18	23155	1286.4		

Treatment Means			
Treatment	Mean	Treatment	Mean
1	488.7	6	564.3
2	520.7	7	503.7
3	536.7	8	465.7
4	490.0	9	567.7
5	507.7	10	498.0

Table 36. Analysis of variance, treatment means, least significant difference sets, and contrast coefficients for infiltration data.

Analysis of Variance					
Source	D.F.	S.S.	M.S.	F-Value	P-Value
Blocks	2	42.3	21.18		
Treatments	10	2267.1	226.71	23.91	.0000
Error	20	189.6	9.48		

Treatment Means					
Treatment	Mean	LSD	Treatment	Mean	LSD
1	1.39	a	6	2.41	a
2	0.92	a	7	0.41	a
3	4.91	a	8	26.71	c
4	2.63	a	9	0.46	a
5	1.57	a	10	1.45	a
			Range	18.42	b

Contrast Coefficients			
Contrast	Coefficients	t	P
Fertilize/non-fertilize	-6,-6,4,-6,-6,4,4,4,4,4,0	3.86	.000
Till/non-till	-9,1,1,1,1,1,1,1,1,1,0	1.72	.101
Irrigate/non-irrigate	-5,-5,-5,-5,5,5,5,-5,5,5,0	-5.38	.000
Plastic covered/non-covered	-4,-4,-4,6,-4,-4,6,-4,6,6,0	-4.42	.000
Till-fertilize-irrigate/others	-4,-4,-4,-4,-4,6,6,-4,6,6,0	-4.50	.000
Calcium chloride/others	-1,-1,-1,-1,-1,-1,-1,9,-1,-1,0	13.29	.000
Mulch/non-mulch	-3,-3,-3,-3,-3,-3,7,-3,7,7,0	-4.09	.000
Peat mulch/straw mulch	0,0,0,0,0,0,-2,0,1,1,0	0.25	.804
Supertillage/others	-2,-2,-2,-2,-2,-2,-2,-2,8,8,0	-1.00	.326

MONTANA STATE UNIVERSITY LIBRARIES



3 1762 10079146 4

