UCLA 12-1301 UC 11, 62

ENVIRONMENTAL EFFECTS OF SOLAR THERMAL POWER SYSTEMS

ENVIRONMENTAL EFFECTS OF HEAT TRANSFER AND STORAGE FLUIDS

PLANT TOXICITY AND MOVEMENT IN SOILS

JULY 1981

PREPARED FOR

U.S. DEPARTMENT OF ENERGY

Contract No. DE-AM03-76-SF00012

LABORATORY OF BIOMEDICAL AND ENVIRONMENTAL SCIENCES UNIVERSITY OF CALIFORNIA, LOS ANGELES

Cat No: 14.1014

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for any third party's use or the results of such use of any information apparatus, product or process disclosed in this report, or represents that its use by such third party would not infringe privately owned rights.

> Printed in the United States of America Available from National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161

> > NTIS price codes Printed copy: \$6.50 Microfiche copy: \$3.50

ENVIRONMENTAL EFFECTS OF SOLAR THERMAL POWER SYSTEMS

ENVIRONMENTAL EFFECTS OF HEAT TRANSFER AND STORAGE FLUIDS

Plant Toxicity and Movement in Soils

H. Nishita and R.M. Haug

July 1981

Prepared for U.S. DEPARTMENT OF ENERGY

Contract No. DE-AM03-76-SF00012 between the U.S. DOE and the University of California

Laboratory of Biomedical and Environmental Sciences University of California, Los Angeles 900 Veteran Avenue Los Angeles, California 90024

ABSTRACT

Field experiments on the movement of several heat transfer and storage oils (Therminol 66, Caloria HT43, and Dow 200) in soil and on the plant toxicity of these materials were conducted at Nevada Test Site. These studies were conducted in an area where the soil is nonsaline and calcareous, and the vegetation is mostly Larrea tridentata with Oryzopsis hymenoides, Ambrosia dumosa, and Lycium andersonii. The abiotic factors (air and soil temperatures, rainfall, and soil moisture tension) were monitored during the experimental period and are discussed. The movement of the oils in the soil was determined in two ways--soil columns in plastic boxes and baresoil plots. In plastic boxes, Therminol 66 moved downward about 6.3 cm Dow 200 moved about 3.8 cm in 281 days and showed virtually in 281 days. no further downward movement to the end of experimental period (555 days). In the bare-soil plots, the limit of downward movement of the oils during the experimental period was 20.6 cm, 18.7, and 14.9 cm for Therminol 66, Caloria HT43, and Dow 200, respectively. The rate of movement was roughly 0.047 cm/day to 16.8-cm depth in 336 days, 0.067 cm/day to 18.7-cm depth in 281 days, and 0.044 cm/day to 14.9-cm depth in 336 days for Therminol 66, Caloria HT43, and Dow 200, respectively. In general, Caloria HT43 showed the greatest movement, while Dow 200 showed the least movement. Of the oils studied, Therminol 66 was the least toxic to native plants, whereas Dow 200 was the most toxic. The toxic effect on plants depended on the growth stage at which the plants were contaminated. Ambrosia dumosa contaminated in its dormant stage was more resistant to the toxic effect of Therminol 66 than when it was contaminated in its green, leafed stage.

ii

TABLE OF CONTENTS

	Page
INTRODUCTION]
MATERIALS AND METHODS	3
RESULTS AND DISCUSSION	7
Environmental Factors	7
Downward Movement of Oils in the Soil Profile	. 8
Plastic Boxes	8
Bare-soil Plots	10
Deleterious Effect on Plants	13
GENERAL DISCUSSION	15
SUMMARY	17
REFERENCES	18

LIST OF TABLES

Table	Title	Page
1	Chemical Properties of Soil JF79	20
2	Field Experiments with Heat Transfer and	
	Storage FluidsPlant Species, Plot	
	No., and Contamination Date	21
3	Attributes of Air Temperature in	
	Jackass Flats, Nevada	22
4	Soil Moisture Tensions (bars) at 7.6-,	
	20.3-, and 61.0-cm Depths	23
5	Particle Size Distribution of Field Plot	
	Soils Contaminated with Different Kinds	
	of Heat Transfer Fluids	24

LIST OF FIGURES

Figure	Title	Page
1	Lucite Box Used to Determine the Movement of Heat Transfer Fluids in Soil	25
2	A Row of Soil Columns (Contaminated by Therminol 66) Buried in Natural Environment	26
3	Bare-soil Plot (2 x 4 m Dimension)Contaminated with Caloria HT43	27
4	Fluid Sprinkler Made of Lucite	28
5	Steel, Soil Core Sampler	29
6	Soil Profile Distribution of Therminol 66 Indicated by Gas Chromatograms	30
7	Soil Temperature at 7.0-, 20.3-, and 61.0- cm Depths	31
8	Rainfall During the Experimental Period, October, 1979 to June, 1981	32
9	Soil Profile Distribution of Therminol 66 in Plastic Boxes	33
10	Soil Profile Distribution of Dow 200 in Plastic Boxes	34

Figure	Title	Page
11	Soil Profile Distribution of Therminol 66 in the Bare-Soil Plot No. 6	35
12	Soil Profile Distribution of Caloria HT43 in the Bare-Soil Plot No. 16	36
13	Soil Profile Distribution of Dow 200 in the Bare-Soil Plot No. 4	37
14	<u>Ambrosia</u> <u>dumosa</u> Plants in the Dormant Phase	38
15	Ambrosia dumosa Plants in April, 1981	39
16	Larrea tridentata Plants in April 1981	40

vi

ENVIRONMENTAL EFFECTS OF HEAT TRANSFER AND STORAGE FLUIDS--PLANT TOXICITY AND MOVEMENT IN SOILS

H. Nishita and R. M. Haug

INTRODUCTION

Within the next several decades, a considerable portion of our national energy needs is anticipated to be met by inexhaustible solar energy. The U.S. Department of Energy has as its goal of displacing by the year 2000 three quads of energy $(3 \times 10^{15} \text{ Btu})$ which would otherwise be provided by non-renewable resources. There are four major types of solar thermal energy systems (STES), e.g., central receivers, parabolic troughs, parabolic dishes, and fixed mirror hemispherical bowls (Baldwin, Steinberg, and Stea 1981), One of the essential components of these systems is "heat transfer fluid" or "working fluid," which absorbs thermal energy from solar radiation. The heated fluid is then transported to a heat engine or exchanger, where the absorbed heat is converted into mechanical energy or process heating. Part of the energy may be diverted and stored in a thermal energy storage subsystem for use at a later time. The desirable properties of heat transfer and storage fluids are determined to some extent by the STES used. Many of the fluids that may be used are toxic, flammable or explosive (Searcy 1978; Kahane et al. 1980; Sandia National Laboratory 1981).

One of the concerns in the use of heat transfer and storage fluids is their possible release into the natural environment through

spills, leaks in operational equipment, accidents, or improper disposal. When any of these events occur, its short and long term impact on the environment needs to be assessed. With this in mind, the objectives of our program have been to determine (1) the rate of degradation and persistence of these materials in soils, (2) the rate of their movement or transport in soils, and (3) the toxicity of these materials (or their degradation products) to plants. These objectives were pursued by laboratory and field experiments.

Several aspects of these objectives have been reported previously. Nishita (1980) reported the plant toxicity threshold levels of several heat transfer and storage fluids and eutectic salts that were determined by using a modified Neubauer technique. Using barley seed germination and seedling growth as toxicity tests, the general order of toxicity of the fluids applied to three different mineral soils was ethylene glycol > Dow 200 >> Caloria HT43 > Therminol 66. The toxicity order of the fluids applied to an organic soil was ethylene glycol > Caloria HT43 > Dow 200 > Therminol 66. With the eutectic salts tested, Dupont HITEC was more toxic than 8.4% NaCl-86.3% NaNO3-5.3% Na2SO4 mixture in three of the four soils used. There was no apparent difference of toxicity between these salt mixtures in the fourth soil. Depending on the fluid and salt mixture, the toxicity threshold levels for barley seedling ranged from 4,451 to 317,488 ppm in the soils used. In another report (Nishita and Haug 1980), the biodegradability of four heat transfer and storage fluids (ethylene glycol, Therminol 66, Caloria HT43, and Dow Corning Fluid No. 200 (Dow 200)) were discussed. Moist fluidcontaminated soils incubated at 28° and 37°C for 8 weeks in the

laboratory showed that ethylene glycol would undergo biodegradation fairly readily. The other three fluids did not show measurable degradation during the experimental period. This implies the potential long term persistence of these materials in natural environment. The present report gives the results of field experiments on the movement of Therminol 66, Caloria HT43 and Dow 200 in soil and the toxicity of these materials to several native desert plants.

MATERIALS AND METHODS

Field experiments were conducted at Jackass Flat in the northern Mojave Desert area of the Nevada Test Site from 24 October 1979 to 2 June 1981. The vegetation of the study area is mostly <u>Larrea</u> <u>tridentata</u> with <u>Oryzopsis hymenoides</u>, <u>Ambrosia dumosa</u>, and <u>Lycium andersonii</u>. The chemical properties of the soil (Soil JF79) in this work area are shown in table 1. It is a nonsaline, calcareous soil.

The heat transfer and storage fluids selected for study were Therminol 66, Caloria HT43, and Dow 200 (200 cS viscosity at 25°C). The first two fluids are hydrocarbon oils, whereas Dow 200 is a silicone oil. The physico-chemical properties of these materials have been compiled by Searcy (1978), Kahane et al. (1980), and Sandia National Laboratory (1981). The fluids used for study were fresh materials as supplied by the manufacturers.

The movement of the fluids in the soil was measured in two ways. In one method, the downward movement was measured in soil columns that were in Lucite boxes. In the other method, it was measured in core

samples taken from contaminated bare-soil plots. In the first method, Lucite boxes (15.2 x 15.2 x 20.3 cm inside dimension) were filled with Soil JF79 that had been passed through 2 mm sieve and were buried in the field soil with the surface exposed to the atmosphere at the surrounding ground level and the bottom open for free drainage. The Lucite boxes were designed so that the soil column in them could be partitioned into 1.27-cm layers by inserting stainless steel slides (0.77 mm thick) into them (Fig. 1). Figure 2 shows a row of these boxes buried in the field. Fifteen of these columns were contaminated with Therminol 66 and 15 with Dow 200. (Caloria HT43 was not set up with Lucite boxes). The surface layer (1.59 cm thickness) of each column consisted of 800 g of contaminated soil. The contamination level of Therminol 66 was 99,950 ppm whereas that of Dow 200 was 96,322 ppm. The contamination level on the areal basis was 344.2 and 331.7 mg/cm^2 for Therminol 66 and Dow 200, respectively. One or two columns were retrieved periodically to determine the downward movement of the oils in the soil. In the second method, bare-soil plots (2x4 m dimension) were contaminated on the surface with 75.7 1 (20 gallons) of Therminol 66, Caloria HT43, or Dow 200 (Fig. 3). The plot area was contaminated as uniformly as possible by using a special sprinkler that was fabricated by our shops section (Fig. 4). The surface application of Therminol 66, Caloria HT43, and Dow 200 amounted to 950, 813, and 918 mg/cm^2 , respectively. The soil core samples were taken periodically with a core sampler (10x10x23 cm inside dimension) (Fig. 5). The sampler was driven into the soil by hammering. The sampler was designed so that the soil core could be partitioned into 1.91 cm (0.75 inch)

depth increments by sliding stainless steel slides (0.77 mm thick) into the slots cut on the sampler walls.

Therminol 66 and Caloria HT43 in the soil were determined on pentane extracts with a Hewlett Packard Model 5880A gas chromatograph with a Level Three terminal. The pentane extracts of the soil were obtained by suspending 10 g of air-dry soil in 25 ml of pentane, mixing the suspension for 30 min on a mechanical mixer and then centrifuging for 10 min at 34,858 gravity. For the Therminol 66 analysis, a 12-m fused silica capillary column (methyl silicone SP2100) was used in the split mode. For the Caloria HT43 analysis, a 25-m column with the same coating was used in the splitless mode. An example of chromatograms of Therminol 66 in a soil profile is given in figure 6.

The concentrations of the oils were calculated by using polynomial equations of the form, $y = Ax^3 + Bx^2 + Cx + b$, fitting standard curves of regression between known concentration of oil in the soil and one of several parameters. The parameters used for this purpose were area under a peak or total chromatogram, or the ratio of the area under selected peak(s) to the area of total chromatogram. The concentration of Therminol 66 in the soil was calculated on the basis of the ratio of whole oil chromatogram area to the total chromatogram area (whole oil + solvent) and on the basis of the ratio of a predominant peak area to the total chromatogram. Two separate calculations were done on the basis of the latter ratio by using two separate peaks. The more dominant one of these peaks had a retention time (RT) of 43,7 min, while the other had RT of 40.6 min. The mean and standard deviations of these three calculations for each soil sample are reported. The concentration

of Caloria HT43 in the soil was calculated on the basis of actual peak areas of three separate peaks. The retention time of these peaks were 48.85, 53.51, and 57.97 min. The mean and standard deviation of these three calculations are reported. With both Therminol 66 and Caloria HT43, the coefficient of variation of the calculated results was <10 percent.

Dow 200 in the soil was determined by measuring silicon content of methyl isobutyl ketone (MIBK) extract with an atomic absorption spectrophotometer (Instrumentation Laboratory 751). Except for the fact that MIBK was used instead of pentane, the method of obtaining soil extracts was the same as for Therminol 66 and Caloria HT43. The unknowns were compared against standards that were prepared by adding known amounts of oil to the soil on a weight basis and extracting them with MIBK in the same manner. An error analysis indicated that soil concentration values between 1.0 and 7.0 percent are within 5 percent of their true values, and those between 0.5 and 1.0 percent are within 10 percent.

Soil moisture tensions and temperatures were measured with Wescor HR33T dewpoint microvoltmeter with the Wescor thermocouple psychrometer/ hygrometer (PCT 55-05) buried at 3, 8, and 24 inches (7.6, 20.3, and 61.0 cm, respectively). The rainfall was monitored with Taylor 28-cm Clear-Vu rain gauge. The air temperatures were monitored with a hygrothermograph equipped with 7-day strip chart.

To study the effect of the heat transfer and storage fluids on plants, miniplots (lxl m square) were set up with Therminol 66, Caloria HT43, and Dow 200. Each miniplot had one growing plant (Larrea tridentata or Ambrosia dumosa) in the center and was contaminated

with 7.6 l of fluid. The fluids were applied to the plant and soil within the one-square meter area as uniformly as possible using the sprinkler shown in figure 4. The application of Therminol 66, Caloria HT43, and Dow 200 was around 760, 650, and 734 mg/cm², respectively. The miniplots were set up in three replications for each plant species and fluid. The <u>Ambrosia</u> plots were contaminated with the fluids in the dormant and in the green-leafed, blooming stages. The <u>Larrea</u> plants, which are perennial, were contaminated only in the green-leafed condition. The contamination date of each field experiment is shown in table 2.

RESULTS AND DISCUSSION

Environmental Factors

During the course of field experiments, rainfall, soil moisture tension, and air and soil temperatures were monitored in order to follow the environmental conditions to which the oil-contaminated plants and soils were exposed. As expected, the air temperature varied with the season of the year (table 3). The highest average daily maximum temperature (36.8°C) occurred in July, 1980, with the observed maximum at 42°C. The lowest average daily minimum temperatures, which ranged from 1.6° to 8.8°C, occurred during the months of October through April. During the entire experimental period, the lowest air temperature (-4.5°C) observed was in October, 1979.

Figure 7 shows the soil temperature at 7.6-, 20.3- and 61.0-cm depths. As with air, the soil also went through a cycle of temperatures during the experimental period. Relatively high temperatures occurred at

all depths during the months of July, August, and September. The highest observed temperature (45°C) at 7.6-cm depth occurred in July, 1980. The relatively low temperatures occurred during the months of November through March. The lowest soil temperature (6°C) was measured in November and in December, 1979, at 7.6-cm and 20.3-cm depths, respectively.

The rainfall data are given in figure 8. The measurable rainfall was very sparse during the experimental period. The greatest rainfall (43.6 mm) occurred on 7 March 1980. The 1980-1981 winter season was relatively dry compared to the 1979-1980 winter season.

Table 4 gives the soil moisture tensions at 7.6-, 20.3, and 61.0-cm depths. The reading dates after recent rainfall are indicated in the table by the letter R. As expected, the soil at 7.6-cm depth was the wettest after rainfall and dried out rapidly thereafter. The moisture tensions recorded as <-60 or less reflect extremely dry conditions. Since rainfall was sparse, the soil was extremely dry the majority of the time during the experimental period.

Downward Movement of Oils in the Soil Profile

Plastic Boxes

Each oil used showed some degree of downward movement in the soil profile over a period of time. Figure 9 shows the distribution of Therminol 66 in the soil columns in plastic boxes. The measurements made on the first collection of soil columns, which was done 63 days after contamination with Therminol 66, showed movement down to about 4.1-cm depth. This is equivalent to a net downward movement of about 2.5 cm during the 63-day period, because the surface 1.6 cm of the columns was

uniformly contaminated with oil at the beginning of the experiment. The sampling done after 150 days showed no apparent change of movement of the oil, even though there was 43.6 mm of rainfall a few days before sampling. The sampling done after 218-day period, showed movement down to 6.7-cm depth, which is equal to about 5.1 cm net movement. The 281- and 338-day samplings showed movement down to 7.9-cm depth. Movement to 9.2-cm depth was indicated by 402-day sampling, but not by the 484-day sampling. Thus, the approximate limit of movement during the experimental period was estimated to be to about 7.9-cm depth (6.3 cm net movement). The rate of movement to this depth is equal to 0.022 cm/day in 281 days.

The downward movement of MIBK-extractable Dow 200 in the soil in plastic boxes is shown in figure 10. The measurements made on the first collection 63 days after contamination showed downward movement to 2.9-cm depth. This indicated a net movement of 1.3 cm, because as with Therminol 66, the surface 1.6 cm of the soil was uniformly contaminated at the beginning of the experiment. The soil column collected 281 days after contamination showed definite downward movement to 5.4 cm depth, indicating a net movement of 3.8 cm. Subsequent soil collections made up to 555 days after contamination showed only slight, if any, downward movement below the 5.4 cm depth. Consequently, this depth appeared to be the approximate limit of movement of Dow 200 during the experimental period. The rate of movement to this limit in 281 days amounts to 0.014 cm/day. Thus, the movement of Dow 200 in the soil was somewhat slower than Therminol 66.

Bare-Soil Plots

Figure 11 shows the profile distributions and downward movement of Therminol 66 in the bare-soil plot No. 6 at various times after contamination. The core collections done 92, 148, and 216 days after contamination showed downward movement to 11.1-cm depth. The collection done 279 days after contamination showed movement to 13.0-cm depth, whereas those done 336, 400, and 482 days after contamination showed movement to 16.8-cm depth. At the end of the experimental period (559 days), the movement was down to 20.6-cm depth. The rate of movement was roughly 0.037 cm/day to the 20.6-cm depth in 559 days.

The profile distributions and downward movements of Caloria HT43 in the bare-soil plot No. 16 is shown in figure 12. The core collections done 37, 93, and 161 days after contamination showed downward movement to 11.1-cm depth. The movement was down to 13.0-cm depth 224 days after contamination. The core collections done 281 and 427 days after contamination showed movement to 18.7-cm depth, but those done after 345 and 504 days showed movement only to 14.9-cm and 16.8-cm depths, respectively. This variation probably was due to the variation of soil texture within the plot. In any case, the limit of downward movement of Caloria HT43 during the experimental period was considered to 18.7-cm, since two samplings showed movement to this depth. The rate of movement to 18.7-cm depth was around 0.067 cm/day in 281 days.

Figure 13 shows the movement of MIBK-extractable Dow 200 in the bare-soil plot No. 4. The core samplings done 92, 148, and 279 days after contamination showed downward movement to 11.1-cm depth. The sampling done 216 days after contamination, however, showed downward

movement only to 9.2-cm depth. As with Caloria HT43, this variation probably was due to soil textural variation within the plot. The samplings done 336, 400, 482, and 559 days after contamination all showed downward movement to 14.9-cm depth. Thus, this depth appeared to be the limit of movement of Dow 200 during the experimental period. The rate of movement was around 0.044 cm/day to 14.9-cm depth in 336 days.

A comparison of the limit of downward movement of Dow 200 (14.9 cm in 336 days) and Caloria HT43 (18.7 cm in 281 days) during the experimental period indicated that the latter moved to a greater depth in shorter Thus, Caloria HT43 moved faster than Dow 200. The limit of time. movement of Therminol 66 (20.6 cm in 559 days) could not be compared because of the large difference of time. However, if comparable time is taken, Therminol 66 movement, which was 16.8 cm in 336 days, was greater than that of Dow 200, which was 14.9 cm in 336 days. By comparing the rate of movement of Therminol 66 (0.047 cm/day for 279 days) and Caloria HT43 (0.067 cm/day for 281 days), the latter oil appeared to have moved faster than the former. The cause of the apparently more rapid movement of Caloria HT 43 has not been determined, but its lower density and viscosity tend to favor it. Its density and viscosity were 0.8587 g/cm³ at 15°C and 29.6 cS at 40°C, respectively (Exxon Corp.), whereas those of Therminol 66 were ~1.002 g/cm³ at 25°C and 30 cS at 37.7°C, respectively (Monsanto Co.). Also, our gas chromatographic data indicated that Caloria HT43 contained molecular weight components ranging from C_{16} to C_{32} , whereas those in Therminol 66 ranged from C_{18} to C_{24} , indicating that the former had lower molecular weight as well as higher molecular weight substances. The lower molecular

weight substances may have migrated more rapidly than the higher molecular weight components. Another influencing factor may have been the soil textural differences among the contaminated plots, but the particle size analyses (table 5) did not support this definitively. Plot 16 (Caloria HT43) had lesser amount of coarse fraction (>2 mm) in the upper profile level (0-7.3 cm) than plot 6 (Therminol 66), but had greater amount of coarse particles in the lower profile level (7.3-14.9 cm). On the other hand, in the <2 mm fraction, plot 16 had greater amount of silt and clay fraction in the upper profile level than plot 6. The higher silt and clay contents should cause greater retardation of fluid movement. Perhaps, a more definitive soil textural effect may have been observed if thinner soil profile layers had been sampled.

The movement of both Therminol 66 and Dow 200 in the plastic boxes were appreciably lower than in the bare-soil plots. Part of this effect may have been the level of contamination. The contamination level of Therminol 66 and Dow 200 in the plastic boxes was 344.2 and 331.7 mg/cm², respectively, whereas on the bare-soil plots, it was 950 and 918 mg/cm², respectively. Another factor is believed to be the textural difference between the soil in the plastic boxes and the soil of the bare-soil plots. The plastic boxes were filled with the native soil that had been passed through a 2-mm sieve. Thus, the soil was texturally and structurally uniform. The bare plots consisted of undisturbed soil in its natural state. Table 5 shows that the plots contained an appreciable percentage >2 mm particle size fraction.

Deleterious Effect on Plants

The oils studied showed varying degrees of toxicity to plants (Ambrosia dumosa and Larrea tridentata) in natural environment. The Ambrosia plants that were contaminated (17 October 1979) with Therminol 66 in their dormant phase showed varying degrees of viability, e.g. production of normal green leaves and blossoms. The viability ranged from about 15 to 50 percent of the morphological structure of the plants during the first spring season following contamination. The plant viability effects may be seen by comparing figure 14 with figure 15. Figure 14 shows the contaminated (no. 11) and uncontaminated (no. 190) Ambrosia plants in their dormant phase. In the following spring (May, 1980) when the plants were out of dormancy, about 50 percent of the morphological structure of the contaminated plant (no. 11) appeared to be viable, whereas the control plant (no. 190) was completely viable. In the 1981 spring, the same contaminated plant (no. 11) showed less recovery (fig. 15). Only about 20 percent of its morphological structure appeared to be viable. Part of this effect may have been due to the lower rainfall and soil moisture status in the 1981 season compared to the 1980 season.

Caloria HT43 was somewhat more detrimental to <u>Ambrosia</u> than Therminol 66. The <u>Ambrosia</u> plants that were contaminated (11 December 1979) with Caloria in their dormant phase showed lesser degree of viability. The first spring (May 1980) following contamination only about 5 to 10 percent of the morphological structure of the contaminated plants showed viability. In the second spring (1981 season) none of

the contaminated plants appeared to be viable.

Dow 200 appeared to be the most detrimental of the oils studied. The <u>Ambrosia</u> plants that were contaminated (17 October 1979) by Dow 200 did not show any sign of viability during the 1980 growth season or during the 1981 season. These results, in general, agreed with laboratory tests, which showed that the soil threshold concentration for plant toxicity of these oils was Dow 200 << Caloria HT43 < Therminol 66 (Nishita 1980). Thus, of the oils studied, Therminol 66 was the least toxic to plants.

The viability of the plants depended on the growth stage at which the plants were contaminated with oils. The <u>Ambrosia</u> plants discussed above were contaminated in their dormant phase. When <u>Ambrosia</u> plants were contaminated in their green, leafed stage, none of them showed sign of viability during the following spring growth season irrespective of the oil applied. Thus, the plants contaminated in their green, leafed stage were more susceptible to the deleterious effect of the oils than those contaminated in their dormant stage.

Larrea tridentata plants showed relatively high sensitivity to the deleterious effect of contaminating oils in comparison to dormant stage of <u>Ambrosia</u>. The <u>Larrea</u> plants that were contaminated in the autumn (October 1979) showed no viability in the following spring growth season even when they were contaminated with Therminol 66, which was the least toxic of the oils applied. These plants did not show recovery even after two spring growth seasons (fig. 16). The sensitivity of <u>Larrea</u> plants probably was due to the fact that it bore green leaves when the

oils were applied. <u>Larrea</u> is a perrenial plant that bears green leaves throughout the year. Aside from the possibility of absorption of some toxic component(s) of the oil, the high susceptibility of the green, leafed plants to injury is believed to be the "frying effect" of the oil due to the heat absorbed from the hot ambient air and solar radiation.

GENERAL DISCUSSION

In the company brochure, Therminol 66 is stated to be practically non-toxic to mammals by ingestion in single doses and by single dermal application (Monsanto). It is a slight eye and a mild skin irritant on prolonged contact. Caloria HT43 is stated to present no special toxicity hazards and can be handled with the simple precautions ordinarily observed with lubricating oils (Exxon 1977). Dow 200 is essentially non-toxic and non-irritating, although temporary discomfort may result if rubbed into the eye (Dow Corning). Dermal application of Dow 200 to human subjects, rabbits and rats resulted in no significant effect (Hobbs et al. 1972). Selected silicone fluids had very low toxicity to daphnia, fresh water fish, marine species, mallard ducks, bobwhite quail, and domestic chickens (Hobbs et al. 1975). Thus, the heat transfer oils used in the present study are practically non-toxic to animals and humans. This may raise some questions as to the causes of the deleterious effects of these materials when applied to plants and soils.

A number of factors can contribute to the deleterious effect of these oils to plants and soils. As mentioned above, the application of oils to plants can have a "frying effect". The combination of oil film on the plant surfaces, hot air temperature, and strong solar radiation

under extremely dry desert conditions can cause this effect. The application of the oils to soils can disrupt the normal soil-plant water and nutrient interrelationships. In this respect, the amount of the oil applied can be a factor. For example, in our previous work (Nishita 1980) using a modified Neubauer technique, up to about 7.9, 6.8, and 0.5 percent by weight of Therminol 66, Caloria HT43, and Dow 200 was tolerated in Soil JF79 without reduction of barley seedling yield. Dow 200 was tolerated in the least amount because it made the soil extremely hydrophobic and difficult to wet. Therminol 66 and Caloria HT43 made the soil difficult to wet only at the higher levels of applications. Water applied to the soil contaminated with Dow 200 simply passed through without appreciably wetting it. This implies that water in the contaminated soil can be insufficient to sustain normal plant growth. Moreover, the transfer of nutrients from oil-coated soil particles to the plant roots is disrupted, since moisture is needed for this to occur. These effects imply that the cultural method used to test the deleterious effects of the oils can be significant. In the Neubauer technique, the plant culture is watered to a constant weight every day, and the added water is restricted within the volume (about 1 pint) of the container. Consequently, the plant roots always have access to water. On the other hand, plants grown in oil-contaminated soil in the field may suffer from insufficient water in the root zone because of the downward drainage of water encouraged by the hydrophobic nature of the oil-coated soil particles. For this reason, the plants grown under field conditions is expected to be more susceptible to the deleterious effects of oil than those grown by the Neubauer technique. Another factor may be involved in the case of the addition of hydrocarbon oils. In this situation, the C/N ratio of the

soil may be greatly increased and the plants, at least temporarily, may suffer from N deficiency.

The present results definitely show that the application of heat transfer oils to plants and soils has deleterious effects. However, definitive experiments remain to be done to determine the relative contribution of the direct toxicity of the oils to plants as opposed to indirect detrimental effects of physico-chemical changes that occur in contaminated soils.

SUMMARY

Field experiments on heat transfer and storage oils (Therminol 66, Caloria HT43, and Dow 200) were conducted in a desert environment at Nevada Test Site. The environmental conditions of the experiments were recorded by monitoring the rainfall, soil moisture tension, and air and soil temperatures. The downward movement of the oils in the soil profile was measured in two ways. In the plastic boxes, the downward movement of Therminol 66 was 6.3 cm during the experimental period of 281 days. The movement of Dow 200 in plastic boxes was 3.8 cm in 281 days. In the bare-soil plots, Therminol 66 moved to a 20.6-cm depth in 559 days. The movement of Caloria HT43 was to 18.7-cm depth in 336 days. For a comparable time period, the movement was Caloria HT43 > Therminol 66 > Dow 200. The movement in the bare-soil plots was appreciably greater than in plastic boxes. The probable causes of this difference were discussed. The deleterious effect of the oils on native plants was Dow 200 > Caloria HT43 > Therminol 66. The deleterious effect on plants depended on the stage of growth at which they were contaminated. Ambrosia dumosa contaminated in its dormant stage was less susceptible to injury than when it was contaminated in its green, leafed stage.

REFERENCES

- Baldwin, J. H., C. Steinberg, and D. Stea. 1981 Community applications of small scale solar thermal energy systems. Laboratory of Biomedical and Environmental Sciences, University of California, Los Angeles. UCLA 12/1279.
- Dow Corning Corportion. (Undated). Information about silicone fluids --Dow Corning 200 Fluid. Brochure Form No. 22-069d-76.

Exxon Corporation. 1977. Caloria HT43. Brochure Lubtex DG-2C.

- Hobbs, E. J., O. E. Fancher, and J. C. Calandra. 1972. Effect of selected organopolysiloxanes on male rat and rabbit reproductive organs. Toxicol. Appl. Pharmacol. 21:45-54.
- Kahane, S. W., D. Marycz, S. Phinney, J. Hill, M. Yamada, and H. Martin. 1980. Worker health and safety in solar thermal power systems. VII. The toxicological and health implications of solar thermal process fluids. Laboratory of Nuclear Medicine and Radiation Biology, University of California, Los Angeles. UCLA 12/1265.

Monsanto Company. (Undated). Therminol 66. Brochure No. IC/FP-64.

- Nishita, H. 1980. An assessment of plant toxicity threshold of several heat transfer and storage fluids and eutectic salts. Laboratory of Nuclear Medicine and Radiation Biology, University of California, Los Angeles. UCLA 12/1264.
- Nishita, H., and R. M. Haug. 1981. Mineralization of carbon during moist incubation of soil JF79 treated with organic heat transfer and storage fluids. Laboratory of Nuclear Medicine and Radiation Biology, University of California, Los Angeles. UCLA 12-1284.

- Sandia National Laboratories. 1981. Solar heating materials handbook. Sandia National Laboratories. DOE/TIC-11374.
- Searcy, J. Q. 1978. Hazardous properties and environmental effects of materials used in solar heating and cooling (SHAC) technologies: Interim handbook. Sandia Laboratories. SAND 78-0842.

Tabl	e 1
------	-----

Chemical properties of Soil JF79

Properties pH (1=1 H₂O suspension) 8.29 Organic C % 0.11 Cation exchange capacity me/100g 16.16 Exchangeable cations me/100g 11.78 Ca 1.70 2.39 Mg ĸ 0.09 Na Lime as CaCO₃ % 0.45 Free iron oxides % 1.40 0.31 E.C. sat. extract mmhos/cm Clay mineral* М

* M = montmorillonite

Table 2

Field experiments with heat transfer and storage fluids-plant species, plot no., and contamination date

Fluid	Plant genus	Plot No.	Contamination date	Remarks
Therminol 66			10/15/79	Soil in Lucite boxes
		6	10/17/79	2x4 m bare soil
	Ambrosia	7	0	dormant
	T#	9	"	11
	. "	11	"	
	Larrea	8	"	green, leafed
		10		
	Ambracia	14 70 76	E /20/70	leafed flavouring
	AUDPOSIC	7070 6564	5/20/79	leated, flowering
	н	7055	••	11 12
Dow 200			10/15/79	Soil in Lucite boxes
		4	10/17/79	2x4 m bare soil
	Ambrosia	2	10/16/79	dormant
	11	12-150	"	11
	11	5	11	n
	Larrea	3		green, leafed
	11	1	11	11 11
	"	13	11	11 11
		15	12/11/79	
	Ambrosia	6876	5/20/79	leafed, flowering
		70-7159 6976	11	11 14
		16	12/11/70	2
Catoria mi43"	 Ambuacia	10	12/11/79	2X4 m Dare SOII
	AMDPUSId	10		
	н	20	ш	11
	Larrea	17	н	areen leafed
	"	19	11	
	11	21	11	n n
Control	Ambrosia	100	10/17/79	
	11	130	11	
	11	190	11	
	11	160	11	
	Larrea	808	11	
	**	401	11	
		505	11	

* Caloria HT43 was not used to contaminate soil in Lucite boxes. It also was not used to contaminate <u>Ambrosia</u> at the leafed, blooming stage of growth.

Month	Minimum	Maximum	Average daily minimum	Average daily maximum	Overall monthly average	Days of records
			0	C		
1979						
October	-4.5	21.2	2.3	14.0	6.5	31
November	-2.0	20.8	2.6	15.6	8.3	30
December	0.0	32.8	8.8	24.0	16.1	31
1980						
January	-2.4	17.4	1.6	11.9	5.9	30
February	-4.1	21.1	2.1	13.6	7.0	27
March	-2.6	18.0	1.6	14.0	7.3	25
April	1.3	23.0	5.4	19.8	12.2	10
May	5.3	31.0	9.4	24.8	17.2	13
June	7.7	38.0	14.4	31.9	23.5	30
July	14.0	42.0	20.4	36.8	29.0	23
August	11.7	41.2	17.0	34.3	24.0	24
September	10.0	35.7	16.2	31.0	23.5	27
October	1.3	36.0	14.6	30.4	21.2	12
November	-1.0	28.0	6.4	20.2	12.0	17
December	-6.7	22.2	2.2	17.2	8.4	31
1981						
January	-4.2	19.7	2.7	14.5	7.6	16
February	-4.0	24.6	1.4	14.4	7.2	24
March	-2.0	20.0	2.2	14.1	7.6	21
April	3.2	34.5	9.7	25.2	18.1	18
May	3.2	35.0	11.8	26.3	19.4	30
June*	15.5	35.4	18.5	32.5	25.8	4

Table 3 Attributes of air temperature in Jackass Flats, Nevada, October 1979 - June 1981

* June 1 through 4

Table 4					
Soil	moisture	tens	ions	(bars)	at
7.6-	, 20.3-,	and 6	1.0-c	m dept	hs

		Depth (cm)				Depth (cm)	
Date 	7.6	20.3	61.0	Date	/.6	20.3	61.0
1979				1980			
10/24	<-71	<-76	-65.2	7/25	<-93	<-83	-36.9
11/1	<-65	<-73	-57.7	8/14	<-79	<-85	-40.9
11/15	< - 75	<-75	-64.0	8/28	<-75	<-76	-42.4
11/27	<-64	<-72	-62.4	9/11 R	-3.2	<-75	-42.5
12/13	<-65	<-69	<-69	10/1	<-73	< - 75	-43.9
12/27 R	-17.3	<-63	-55.3	10/27	<-64	<-69	-46.1
1980				12/3	-10.7	<-69	-53.3
1/10 R	-14.7	-26.7	0	1 981			
1/28 R	0	-5.3	54.0	1/7	<-67	<-64	-51.2
2/28	0	-2.9	-0.8	1/22	<-60	<-60	-53.6
4/1	-1.1	-0.5	-1.3	2/4 R	-2.9	<-64	-54.0
4/29 R	-13.6	-9.2	-0.4	3/4 R	0	-3.6	<-80
5/20 R	-20.1	-13.9	-14.3	6/2 R	-8.4	-5.2	-25.6

R indicates the dates of mesaurement after recent rainfall (see Fig. 7). Rainfall was measured also on 2/14/80, 2/20/80, and 3/7/80, but soil moisture tensions were not measured on these dates.

Table 5

Particle size distribution of field plot soils contaminated with different kinds of heat transfer fluids

Plot no.	Contaminant	Profile level*	Gross Fi >2mm	ractions <2mm	Particle : Sand	sizes in <2mm Silt	fraction Clay
					- percent-		
4	Dow 200	upper	17.89	82.11	73.53	18.47	8.00
		lower	14.51	85.49	67.51	19.30	13.19
6 Therminol 66	Therminol 66	upper	13.03	86.97	76.43	16.07	7.50
		lower	10.89	89.11	76.12	13.33	10.55
16	Caloria HT43	upper	11.55	88.45	75.02	16.54	8.44
		lower	14.84	85.16	72.98	14.88	12.14

* Upper soil profilelevel = 0-7.3 cm depth. Lower level = 7.3-14.9 cm depth.



Fig. 1. Lucite box used to determine the movement of heat transfer and storage fluids in soil. It is completely open at the bottom.



Fig. 2. A row of soil columns (contaminated by Therminol 66) buried in natural environment. The stakes mark the sites of the columns. The columns are covered with screens to prevent them from being disturbed by animals. Some of the columns have already been retrieved for measurement of fluid movement.



Fig. 3. Bare soil plot (2x4 m dimension) contaminated with Caloria HT43. The wooden stakes within the plot indicate the spots where core samples had been taken already.



Fig. 4. Fluid sprinkler made of Lucite. The rate of flow is adjustable by turning the movable, inner plate at the bottom of the sprinkler.



Fig. 5. Steel, soil core sampler.



Fig. 6. Soil profile distribution of Therminol 66 indicated by gas chromatograms. The surface layer (1) was 1.6 cm deep. Layers 2 through 7 were in 1.27 cm depth increments.



Fig. 7. Soil temperature at 7.0-, 20.3-, and 61.0-cm depths.

 $\underline{\alpha}$









ယ္သ



* Collection date ** Days elapsed

Fig. 10. Soil profile distribution of Dow 200 in plastic boxes.



Fig. 11. Soil profile distribution of Therminol 66 in the bare-soil plot no. 6.

မ္မာ







Fig. 13. Soil profile distribution of Dow 200 in the bare-soil plot no. 4.



Fig. 14. <u>Ambrosia dumosa</u> plants in the dormant phase. In the dormant stage, the plants are leafless and whitish gray in color. The plant on the left (no. 11) was contaminated with Therminol 66 on 17 October 1979. The plant (no. 190) on the right was not contaminated.



Fig. 15. <u>Ambrosia dumosa</u> plants in April 1981. The left plant (no. 11) was contaminated with Therminol 66 on 17 October 1979 when it was in dormancy. Only about 20 percent of its morphological structure showed viability and bore green leaves, whereas the entire uncontaminated plant (no. 190) bore green leaves.



Fig. 16. <u>Larrea tridentata</u> plants in April 1981. The left plant was contaminated with Therminol 66 on 17 October 1979. It is dead with some shriveled brown leaves still attached to the stems. The plant on the right was not contaminated. It shows dark green leaves and has an undergrowth of <u>Oryzopsis hymenoides</u>. The contaminated plot shows no undergrowth of plants.