UC 11, 62

ENVIRONMENTAL EFFECTS OF SOLAR THERMAL POWER SYSTEMS

EFFECT OF SEVERAL THERMAL TRANSFER/STORAGE FLUIDS ON BARLEY SEED GERMINATION AND SEEDLING GROWTH

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ABSTRACT

Plant toxicity threshold level of used thermal transfer/storage materials (Therminol 66, Caloria HT43, Syltherm 800, and Partherm 430) in four different soils was determined by using a modified Neubauer technique. The plant toxicity threshold level of toluene, which is a leading candidate for engine working fluid, was also determined. In three of the soils (Aiken c.l., Yolo c.l., and Egbert muck), the material tolerated in the least amount was Syltherm 800 and that tolerated in the greatest amount was Caloria HT43 from the Coolidge and Willard projects. In the fourth soil (Soil JF79), the material tolerated in the least and in the greatest amount was Partherm 430 and toluene, respectively.

Some chemical analyses of thermal transfer/storage materials were also done. Of the elemental contaminants (Al, Fe, Mn, Co, Cr, Zn, Cu, Cd, Pb, and Ni) determined only a few occurred in concentrations greater than 10 mg/l of oil or 10 μg/g of salt material. These elements were Al in Dow 200, Therminol 66 (Sandia) and Syltherm 800; Fe in Syltherm 800; and Cr and Zn in Partherm 430. Free fatty acids and organic peroxides contents of the used oils were very low, indicating that the heating to which the oils were subjected did not cause appreciable oxidation. Exposure to natural elements (direct solar radiation, ambient air and temperature) for an extended period of time (up to 2 months) appeared to cause more oxidation of the oils than heating alone.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

EFFECT OF SEVERAL THERMAL TRANSFER/STORAGE FLUIDS ON BARLEY SEED GERMINATION AND SEEDLING GROWTH

H. Nishita and R. M. Haug

INTRODUCTION

In the next decade, several large solar thermal energy conversion facilities are expected to be developed. These facilities may employ a distributed receiver configuration or a central receiver system to collect the solar energy. The distributed receiver refers to a system which employs multiple collection centers for solar radiation as opposed to the single collection point used in the central receiver system (ERDA 1977). In either system, a thermal transfer fluid that absorbs and transports the solar thermal energy to an engine or heat exchanger is an essential component. A secondary working fluid may be required to drive the engine. A portion of the thermal transfer fluid stream may be directed to a heat exchanger in a thermal storage subsystem. In some systems all of these functions can be accomplished by the same fluid. Consequently, fluids used in solar thermal energy systems are generically thermal transfer/storage fluids.

One of the concerns in the use of thermal transfer/storage fluids is the release of these materials into the environment through spills, leaks in operational equipment, accidents, or improper disposal. Because of this, studies on certain environmental effects of selected thermal transfer/storage fluids have been initiated. Our previous reports discussed the biodegradability of several organic thermal transfer/storage fluids in the soil (Nishita and Haug 1981a), and their movement in the soil and toxicity to native plants (Nishita and Haug 1981b). Another of our reports (Nishita 1980) discussed the plant toxicity threshold of a glycol fluid, a silicone oil, two hydrocarbon oils, and two eutectic salt mixtures. All of these previous reports were concerned with experiments done with fresh materials (materials that were received directly from the manufacturers and had not been used in any solar thermal energy system). The present report is concerned with plant toxicity threshold of thermal transfer/storage oils that have actually been used in solar thermal energy systems. Used oils are of interest, since they may contain degradation products and system-derived heavy metal contaminants that affect plant growth. Chemical analyses of some of these degradation products and contaminants are included. This report is also concerned with plant toxicity of one eutectic salt mixture (Partherm 430) and one of the likely candidates for a Rankine cycle working fluid (toluene). Several experiments on the degradation of thermal heat transfer/storage oils due to heat and solar radiation are also discussed.

MATERIALS AND METHODS

Four widely different types of soils (Aiken clay loam, Yolo clay loam, Soil JF79, and Egbert muck) were used for this study. Aiken c.l. is a moderately acidic, kaolinitic soil collected near Paradise, California. Yolo c.l. and Soil JF79 are montmorillonitic soils collected near Davis, California and in the northern Mojave Desert area of the Nevada Test Site, respectively. Egbert muck is a saline organic soil collected in the Sacramento-San Joaquin River Delta area of California. The chemical properties of these soils were reported previously (Nishita 1980).

The used thermal transfer/storage materials that were studied were those that had been actually used in solar thermal energy systems. These materials are listed with their sources and use histories in table 1. The fresh, unused materials (Therminol 66, Caloria HT43, and Dow Corning Fluid 200 (Dow 200)) that were used for thermal degradation studies were obtained directly from the manufacturers.

Therminol 66 is a synthetic, hydrocarbon oil. Its physico-chemical properties are compiled in several reports (Searcy 1978, Kahane et al. 1980; Sandia National Laboratories 1981) and in the manufacturer's brochure (Monsanto). Caloria HT43 is a stable paraffinic base stock fortified with a temperature oxidation inhibitor (Exxon Corp. 1977). It is a by-product of refinery and varies in composition batch to batch, but is more than adequate as a heat transfer fluid (McCullock 1981). Its typical properties have been compiled (Searcy 1978; Kahane et al. 1980; Sandia National Laboratories 1981; Exxon Corp. 1977). Syltherm 800 and Dow 200 are silicone oils (modified dimethyl siloxane polymers). Their properties are discussed in the company brochures (Dow Corning Corp. 1980 (Undated)). Partherm 430 is an eutectic salt mixture of $NaNO_3$ and KNO_3 in a 60:40 weight ratio. Its properties are discussed in the manufacturer's bulletin (Park Chemical Co.). In addition to thermal transfer/storage materials, one engine working fluid (organic Rankine cycle) was studied. Fresh, unused reagent-grade toluene was selected for this purpose.

Barley seed germination and seedling growth were tested by using a modified Neubauer technique (Nishita 1980). In the procedure, 100 barley seeds (Hordeum vulgare, "Atlas") were placed directly on the surface of fluid-contaminated soil-sand layer and then covered with 100 g of uncontaminated acid-washed sand (size 16). In the original Neubauer technique, 100 rye seeds were planted in the 150-g sand layer that was placed above the soil-sand layer (Kitchen 1948). Thus, in the present technique, the germination of the barley seeds was constrained to occur on the surface of the contaminated soil-sand layer rather than in the sand above the soil-sand layer. Each run was for 21 days in a controlled-environment growth chamber under 12-hours day/night regime. The temperature ranged between 19^0 to 24^0C during each day, except one run which is discussed in the text. The amounts of fluid or salt applied to the soils are indicated in figures 1 through 3. After the initial 5 days, each pot was watered by weight to bring the soil to field capacity every day. All treatments were in triplicate. Because of the limited capacity of the growth chamber, each material was tested in a separate run. The barley seeds used showed a germination test score of 98 percent.

Gas chromatographic analyses were done by the use of Hewlett Packard Model 5880A apparatus equipped with level III terminal and FID detector. For Caloria HT43 chromatograms, a 50 m SP2100 fused silica capillary column was used in the splitless mode. Reagent grade pentane was used as solvent for Caloria HT43. For Therminol 66, a 12 m SP2100 fused silica capillary column was used in the split mode. The solvent was reagent grade xylene. The apparatus operating parameters used to get the chromatograms of Caloria HT43 and Therminol 66 are given in table 2. The correlation between retention time and hydrocarbon chain length was determined by using a boiling point calibration sample (Part No. 5080-8716) obtained from Hewlett Packard.

The free fatty acids in the thermal transfer/storage oils were determined by a modified method of Association of Official Agricultural Chemists (1945). In this procedure, 10 ml of oil was mixed with 50 ml of solution A. This mixture was then titrated with standard 0.1 N NaOH until a permanent faint pink color appeared and persisted for at least 1 min. The amount of the 0.1 N NaOH used in the titration was converted by calculation to express the free fatty acid content of the oil as percent oleic acid. Solution A was a 1 vol methanol/10 vol ethanol mixture titrated to a faint pink color with 0.1 N NaOH using a phenolphthalein indicator. The organic peroxide determination was done by the procedure of Wneeler (1932). In the procedure, 3 to 10 g of oil are dissolved in 50 ml of solvent mixture (60 percent glacial acetic acid, 40 percent chloroform) and 1 ml of saturated KI solution added. Exactly one minute after the addition of KI, 100 ml of water are added and the liberated I is titrated with 0.1 N or 0.01 N sodium thiosulfate. Starch is added toward the end as an indicator.

The chemical determination of Al, Fe, Mn, Co, Cr, Zn, Cu, Cd, Pb, and Ni in thermal transfer/storage materials was done by inductively coupled plasma spectroscopy. The hydrocarbon oils were prepared for analyses by a dry-wet ash procedure. The oils were aliquoted into Pt crucibles, evaporated to dryness and carbonized on the hot plate, ignited in a preheated muffle furnace at 600^{0}C for 30 minutes, and digested with 25 ml HNO_3-15 ml HF-5 ml $HClO_4$ mixture. The silicone oils were evaporated to dryness on the hot plate and then repeatedly (up to 7 times) digested by the HNO_3-HF-$HClO_4$ mixture. Soil salinity was determined on saturation paste extracts according to U.S. Salinity Laboratory Staff (1954).

RESULTS

Caloria HT43 (Coolidge)

Caloria HT43 (Coolidge) was used at Coolidge Solar Irrigation Project. It was used about 17 months above 400°F (204.4°C) with about 540 hours at 550°F (287.8°C) (table 1). This oil did not have any appreciable effect on barley seedling yield by the modified Neubauer technique up to about 3.37 percent concentration in Soil JF79 (Fig. 1). The seed germination at this level was decreased slightly to 97 percent (table 3). In Aiken c.l., there was no appreciable effect on the barley seedling yield up to about 13.50 percent, but seed germination was reduced to 94 percent at this concentration. With Yolo c.l., the fluid was tolerated without appreciable effect up to about 6.74 percent, but seed germination was reduced to 92 percent at this level. In the organic soil, Egbert muck, the oil had no appreciable effect on seedling yield or seed germination even at 20.20 percent concentration, indicating that it was less deleterious in organic soil than in the mineral soils. In the soils studied, the general order of tolerance of this oil without deleterious effect was Soil JF79 < Yolo < Aiken < Egbert.

Caloria HT43 (Willard)

This oil was used at Willard Solar Irrigation Project. Its use history is given in table 1. This oil did not have an appreciable effect on barley seedling yield up to about 3.40 percent concentration in Soil JF79 (Fig. 1). At this concentration, the seed germination was reduced slightly to 97 percent (table 3). At the next higher oil application level (6.80 percent), it was reduced to 89 percent. In Aiken c.l. and Yolo c.l., the barley seedling yields were unaffected up to about 13.60 and 6.80 percent, respectively. The seed germination at these concentrations were slightly decreased to 96 and 97 percent for Aiken c.l. and Yolo c.l., respectively. In Egbert muck, the oil had no appreciable effect on seedling growth up to about 2.40 percent concentration, but seed germination was reduced to 96 percent at this level. In general, the amounts of this oil tolerated in different soils without appreciable effect on barley seedling growth were about the same as for Caloria HT43 (Coolidge).

Although the plant injury threshold for the two different sources of oil were approximately the same, the seedling yield response was somewhat different. At the lower levels of oil application to the mineral soils, the Caloria HT43 (Willard) produced higher seedling yields than Caloria HT43 (Coolidge). At the higher levels, no appreciable yield difference occurred between the two oils. The higher seedling yields at lower application levels of the Willard oil is believed to have been caused by the temporary change of environmental condition. During this plant growth period a break-down of the air-conditioning system of the growth chamber occurred. This break-down caused the exposure of the seedlings to higher temperature (∿30°C during the day-time cycle) than under the routine operating temperature, which was ∿24°C during the day-time cycle. This persisted for 7 days (during the second week of plant growth), while the air-conditioning system was under repair. The plants were exposed to the routine operating temperatures during the first and the third week of the plant growth period.

Therminol 66 (Sandia)

This sample of Therminol 66 was obtained from Sandia National Laboratory. Its use history is given in table 1. This used oil did not have any effect on barley seedling yield up to about 4.00 percent concentration in Soil JF79 and Yolo cl.1 (Fig. 2). At this concentration, seed germination was unaffected in Yolo c.l., but was reduced slightly to 97 percent in Soil JF79 (table 4). At the 7.96 percent level, seed germination was reduced to 53 and 97 percent in Soil JF79 and Yolo c.l., respectively. With Aiken c.l., the seed germination and seedling yield were unaffected up to about 7.96 percent concentration. Above this level, the seedling yield was reduced, but seed germination was unaffected up to about 15.80 percent level. With Egbert muck, the seed germination and seedling yield were unaffected up to about 0.49 percent concentration. Above this level, seed germination was unaffected up to about 15.8 percent, but seedling yield was reduced. Note that although the threshold level at which seedling yield reduction occurred was at a lower level in Egbert muck than in the mineral soils, the actual seedling yield was appreciably greater for Egbert muck than for the mineral soils at all levels of oil application. This effect, perhaps, indicated the higher nutritional status of Egbert muck.

Syltherm 800 (Sandia)

This used oil was also obtained from Sandia National Laboratory (table 1). This oil did not affect the barley seedling yield up to about 3.71 percent concentration in Soil JF79 (Fig. 2), but at this level, the seed germination was slightly reduced to 97 percent (table 4). Above 3.71 percent, both seed germination and seedling yield were sharply reduced. With Aiken c.l., Yolo c.l., and Egbert muck, the barley seedling yield was reduced at concentration equal to or greater than 0.45 percent. The seed germination, however, was unaffected up to about 7.43 percent in Aiken c.l. and to about 3.71 percent in Yolo c.l. With Egbert muck, the seed germination was reduced at all levels of oil application. In general, this oil reduced the seedling yields appreciably more in the organic soil than in the mineral soils. This may be seen readily in table 5, which shows that the ratios of the treatment seedling yield (T) to the control seedling yield (C) were lower for Egbert muck than for the mineral soils. This effect may be due to the difference of interaction of this oil with the soil mineral components as compared to the soil organic matter. The organic C contents of the mineral soils were less than

2.14 percent, whereas that of Egbert muck was 19.12 percent. Syltherm 800 appeared to have more deleterious effect on plant growth than Therminol 66 or Caloria HT43 in Egbert muck as compared to the mineral soils. This is indicated by the fact that with the application of Therminol 66 (Fig. 2) or Caloria HT43 (Fig. 1), the barley seedling yields were generally greater for Egbert muck than for the mineral soils, whereas with Syltherm 800, the seedling yields were vice versa between the two types of soils.

Toluene

The heat from solar thermal systems can be converted to work through Rankine cycle heat engine. In the Rankine cycle, a pressurized fluid is vaporized and expressed through a turbo expander which may be coupled to a mechanical device such as an electric generator. In most solar thermal applications, the Rankine cycle fluid would be heated and vaporized indirectly by a heat transfer fluid which circulated between solar receivers and heat exchangers. The heat of the transfer fluid is transferred to the Rankine cycle fluid in the heat exchangers (Kahane et al. 1980). At present, toluene is the leading candidate for use as an organic Rankine cycle fluid (McCulloch 1981).

Figure 3 shows the barley seedling yield in four different soils contaminated with toluene. The toxicity threshold for Soil JF79 and Yolo c.l. was around 8.00 and 4.00 percent, respectively. With Aiken c.l., slight decrease of seedling yield occurred at 0.50 percent, but marked decrease in yield did not occur until the level of fluid contamination was around 8.00 percent. In view of the small, but definite reduction of yield at 0.50 percent, this level was considered to be the threshold. With Egbert muck, the seedling yield threshold was definitely around 0.50 percent, but seed germination was not affected even at the highest level of fluid application used. The order of tolerance of this fluid in the soils studied was Aiken, Egbert << Yolo < Soil JF79.

Partherm 430

Partherm 430, which is a 60:40 weight mixture of $NaNO_3$ and KNO_3, was obtained from Sandia/Livermore Laboratory. Its use history is given in table 1. This salt mixture increased the barley seedling yield of every soil studied up to the application level of about 1.20 percent (Fig. 3). The seed germination at the 1.20 percent application level was not reduced in Aiken c.l. and Egbert muck, but was reduced slightly in Soil JF79 and Yolo c.l. (table 6). Up to 1.20 percent, the seedling response to the application of the salt mixture varied with the kind of soil. The mineral soils showed progressive increase of seedling yield with increasing salt application at least up to around 0.80 percent, whereas the organic soil showed more or less constant seedling yield increase irrespective of the level of salt application. The increase of seedling yield upon the application of the salt was not unexpected, since K and N are common fertilizer elements. Above 1.20 percent salt application level, all soils showed reduction of seedling yield and seed germination. As discussed later, this reduction is believed to be due to the fact that the deleterious effect of high soil salinity overwhelmed the beneficial effect of K^+ and NO_3^-.

Elemental Contaminants in Used Thermal Transfer/Storage Materials

In order to determine whether or not the thermal transfer/storage materials used contained elemental contaminants that might affect plant growth, the following elements were determined: Al, Fe, Mn, Co, Cr, Zn, Cu, Cd, Pb, and Ni (table 7). In determining whether or not sufficient contaminant was present to affect plant growth, an assumption was made that if the contaminant concentration in the thermal transfer/ storage material was equal to or less than 10 mg/l or 10 µg/g, toxic amounts of the contaminant had not been applied even at the highest level of fluid or salt application to the soil. It is recognized that this criterion is only a rough approximation, because toxic level of elements in soils varies over a broad range. In any case, using this criterion, table 7 shows that only few elements were in concentrations above the assumed critical level. These elements were Al in Dow 200, Therminol 66 (Sandia), and Syltherm 800; Fe in Syltherm 800; and Cr and Zn in Partherm 430. Perhaps, Partherm 430 is noteworthy in that it contained 172.80 and 14.80 µg/g of Cr and Zn, respectively.

Free Fatty Acids and Organic Peroxides in Used Oils

As indicated in table 1, the used oils studied were exposed to various heat regimes. This raised a question as to what effect heating of the oils for an extended period of time at high temperatures might have on their chemical properties. In this respect, our particular interest was in organic acids and organic peroxides, since they may be formed in oils through oxidation and are also injurious to plants when applied to them in sufficient concentration (Johnson and Hoskins 1952).

Table 8 shows that the used Caloria HT43 oils (Coolidge and Willard) contained no detectable amount of free fatty acids, whereas the used Therminol 66 and Syltherm 800 contained small amounts of them. As for the peroxides, Caloria HT43 (Coolidge) contained a small amount (0.04 μmol/g oil), but they were not detectable in Caloria HT43 (Willard). Therminol 66 contained 0.14 μmol/g of peroxides, whereas Syltherm 800 did not have detectable amount of them. The presence of only small amounts of organic acids and peroxides indicated that heating to which these oils were subjected did not cause appreciable oxidation. This, in turn, implies that the growth of barley seedlings in the present study was not affected to any appreciable extent by organic acids and peroxides.

Oxidation of Fresh, Unused Oils

Further effects of heating were studied by using fresh, unused Caloria HT43 and Therminol 66. In this study, the oils were heated in open beakers (exposed to air) on hot plates. Figure 4 shows gas chromatograms of Caloria HT43 that had been through several heating regimens under this condition. The sample that had been heated at 80°C, 20 h/wk (4 h/d, 5 d/wk) for 7 weeks showed marked decrease of the peak heights compared to those of the control. The sample that was heated at 160°C, 20 h/wk (4 h/d, 5 d/wk) for 4 weeks showed greater decrease of peak heights. In fact, a number of peaks have disappeared, even though the operational parameters of the gas chromatograph were the same as those for the control sample. These changes are also shown quantitatively in table 9 in terms of the area under each peak. The decrease of peak areas corresponded to the decrease of peak heights. The decrease of peak heights obviously indicated that chemical changes did indeed take place, but the nature of these changes remains to be determined. Perhaps, one of the causes for the dimunition of peak heights was loss due to volatilization. Some of the compounds that may be involved in this process may be surmised from table 10, which shows the correlation of retention time and normal hydrocarbon chain length. According to table 10, normal hydrocarbon compounds from C_6 up to C_{20} appear to be represented in the chromatogram of Caloria HT43 control sample (Fig. 4). The chemical changes that occurred depended on the kind of oil. Therminol 66 taken through the same heating regimens as that of Caloria HT43 showed relative less marked decrease of peak heights (Fig. 5) and peak areas (table 11).

Except for the formation of peroxides in Therminol 66, only a small degree of oxidation appeared to have occurred under the condition of the experiment. Therminol 66, under treatment B (80°C, 20 h/wk, 7 wk) showed an appreciable amount (20.21 μmol/g) of organic peroxides, but no detectable amount of free fatty acids (table 12). Under treatment C, (160°C, 20 h/wk, 4 wk), it showed a relatively small amount (1.19 μmol/g) of organic peroxides and some (1.31 percent) free fatty acids. The control (treatment A) sample showed 1.31 μmol/g of peroxides, but no free fatty acids. Caloria HT43 showed 1.91 μmol/g of peroxides under treatment B and trace amount under treatment C. No detectable amount of free fatty acids was present under either treatment. Neither the peroxides nor the free fatty acids were present in the control sample. In general, Caloria HT43 was more stable to oxidation than Therminol 66, perhaps because of some unspecified antioxidant in it. The generally lower amounts of peroxides found under treatment C than under treatment B probably were due to some degree of direct thermal decomposition of peroxides at the higher temperature of treatment C. Some evidences for this have been given by Denison (1944), who has shown the decomposition of organic peroxides in petroleum under high temperatures.

Aside from just heating in open beakers, an experiment wherein the fresh oils (Therminol 66, Caloria HT43, and Dow 200) were exposed to natural elements (daily cycle of solar radiation and darkness, ambient air and temperature) for extended periods of time in open beakers was also conducted. An appreciable amount of free fatty acids was formed in Therminol 66, while a lesser amount was formed in Caloria HT43 (table 13). No detectable amount of free fatty acids was found in Dow 200. As for the peroxides, a considerable amount of them (31.11 μmol/g oil) was formed in Therminol 66 under treatment D (exposure to natural elements for 1 month). Under treatment E (exposure for 2 months), a lesser amount of peroxides (28.91 μmol/g oil) appeared to have been formed, indicating perhaps some degree of decomposition or conversion of the peroxides to other chemical forms over a period of time. Compared to Therminol 66, only a small amount of peroxides was formed in Caloria

HT43 and Dow 200. In general, the susceptibility of the oils studied to oxidation under direct solar radiation was Therminol 66 > Caloria HT43 > Dow 200. By comparing the data shown in table 12 with those in table 13, it is evident that the exposure of Therminol 66 and Caloria HT43 to direct solar radiation (together with accompanying temperature) was more effective in causing oxidation than exposure to heating alone. This implies the importance of direct solar radiation in the degradation of these oils in the event of their release into natural environment.

DISCUSSION

The plant toxicity threshold level was considered as the critical fluid or salt concentration above which significant decrease of seed germination and/or plant growth in the contaminated soil will occur. The threshold level may also be considered as the critical concentration below which a given substance may be tolerated without significant deleterious effect on plant growth.

The approximate threshold levels of the materials tested are summarized in table 14. In three of the soils (Aiken, Yolo, and Egbert), the material tolerated in the least amount was Syltherm 800 and that tolerated in the greatest amount was Caloria HT43 (Coolidge and Willard). In Soil JF79, the material tolerated in the least and in the greatest amount was Partherm 430 and toluene, respectively. The generally low tolerance for Syltherm 800 is believed to be due primarily to its effect on the physico-chemical properties of the soil. This material rendered the soil particles hydrophobic and extremely difficult to wet. The water repellency property of this material very likely interfered with the soil-plant-water-nutrient interrelation in the soils. At high levels of application, the hydrocarbon oils also caused some degree of water repellency in the soils, but to a much lesser degree than Syltherm 800.

The tendency of Caloria HT43 (Coolidge and Willard) to be tolerated more than Therminol 66 is of some interest in view of the fact that in our previous work (Nishita 1980) with fresh thermal transfer/storage oils, Therminol 66 was tolerated consistently in greater amounts than Caloria HT43. Direct comparison between these used and fresh materials can not be done, because the used materials may have come from different fresh batches. The results, however, may suggest that the heat regimes to which the used materials were exposed had an influence. This is corroborated to some degree by the data in tables 8 and 12, which show that Therminol 66 was more susceptible to oxidation than Caloria HT43.

Partherm 430 was tolerated considerably less than the hydrocarbon oils, even though the nitrate in it had beneficial effect. This was due to soil salinity. Table 15 shows that the soil salinity (as measured by electrical conductivity of soil saturation paste extracts) increased with increasing application of Partherm 430. Soils with electrical conductivity of saturation paste extracts of 4 mmhos/cm or greater are classified as saline (U.S. Salinity Laboratory 1954). The amount of salt contents of soils above which plant growth is affected depends upon such factors as soil type, salt composition, and plant specie. In the present situation, there appeared to be a delicate balance between the beneficial effect of K^+ and NO_3^- and the deleterious effect of salinity. Initially, the beneficial effect of the former overrode the deleterious effect of the latter. Then at the threshold level, the balance was reversed. An additional factor may have been the high Cr level at the threshold level. The Cr content of the used Partherm 430 was 172.80 μg/g (table 7).

The plant toxicity threshold level depends on the method used to determine it. In the present study, a modified Neubauer technique was employed. This is an intensive soil cropping method in which the roots are constrained to be in contact with soil-sand mixture in a small container. The soil-sand mixture is watered to field capacity daily, and the plants are grown in near optimal environmental condition for plant growth. The plant toxicity threshold levels determined under these conditions are higher (greater amount of toxic materials is tolerated) than those determined by the field culture technique in which free drainage of irrigation water usually occurs. Under field conditions, the moisture status of the soil would be lower than under the conditions of the Neubauer technique. For example, in the extreme situation of silicone oil contamination, the soil may even be dry because of the water repellent characteristic of the silicone-coated soil particles. The water repellency of the silicone-coated particles also causes enhanced drainage of irrigation water from the contaminated zone. Under these stressful conditions, the plant toxicity threshold level for the contaminant would certainly be very low. Thus, the toxicity threshold level as determined by the Neubauer technique probably is the upper limit of tolerance that can be expected for any given contaminant.

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Table 1

Used thermal transfer/storage materials that were obtained from various sources

Used Material	Amount Obtained	Source	Use History
Therminol 66	5.5 l	J. E. Cannon (Sandia)	Used 9 hours/day, 5 days week. Time of use split equally at 100, 200, 300°C. Of the 35 to 40 gallons in use, 12 gallons are changed each month.
Syltherm 800	5.5 l	J. E. Cannon (Sandia)	Normally used at 700°F, with a peak temperature of 750°F. The present sample probably had 40 to 50 hours at approximately 750°F.
Caloria HT43 (Coolidge)	3.9 l	L. Torkelson (Sandia) D. L. Larson (Univ. of Arizona)	Used about 17 months above 400°F with about 540 hours at 550°F. Used at Coolidge Solar Power Plant.
Caloria HT43 (Willard)	7.6 l	D. L. Fenton (New Mexico State Univ.)	Used intermittently for 3 1/2 years at Willard Solar Irrigation Project for a total of 830 hours with the Acurex array and 740 hours with the Solar Kinetics array. The Accurex outlet temperature was about 400-410°F, while that of Solar Kinetics was routinely 450°F. About 2/3 of the oil was heated by Solar Kinetics array and the remaining 1/3 by the Acurex array.
Partherm 430	453 g	R. Carling (Sandia/Livermore)	Sample held at 600°C for about 1200 hours. Used to study the mechanical strengths of materials in contact with molten salt.

Table 2

Operating parameters for gas chromatographic analysis of Caloria HT43 and Therminol 66

Parameter	Caloria HT43	Therminol 66
Injector temperature	220°C	275°C
Detector temperature	220°C	275°C
Temperature program	20-70C at 5°C/min, held at 70°C for 10 min, 70-110°C at 5°C/ min, 110-140°C at 0.5°C/min, 140-180°C at 0.25°C/min held at 180°C for 90 min	80°C for 2 min, 80°-260°C at program rate of 2.5°C/min, held at 260°C for 10 min
Chart speed	0.5 cm/min initially, 0.1 cm/min after 40 min run time	0.5 cc/min
Attenuation	256 initially, 1 after 22 min run time	256 initially, 16 after 5 min
Threshold	4	1
Peak width	0.64 min	0.04 min
Gas flow rate	He, 28 cc/min	He, 28 cc/min

Table 3

Average percentage of seed germination at various application levels of Caloria HT43 (Coolidge) and Caloria HT43 (Willard) to four soils

Fluid material	Soil	Level of fluid application %	Average seed germination %
Caloria HT43 (Coolidge)	Soil JF79	0-1.70	98
		3.37	97
		6.74	88
		13.50	14
		20.20	9
	Aiken	0-6.74	98
		13.50	94
		20.20	61
	Yolo	0-3.37	98
		6.74	92
		13.50	46
		20.20	23
	Egbert	0-20.20	98
Caloria HT43 (Willard)	Soil JF79	0-1.76	98
		3.40	97
		6.80	89
		13.60	17
		20.40	8
	Aiken	0-6.80	98
		13.60	96
		20.40	63
	Yolo	0-3.40	98
		6.80	97
		13.60	44
		20.40	12
	Egbert	0-13.60	98
		20.40	96

Table 4

Average percentage of seed germination at various application levels of Therminol 66 and Syltherm 800 to four soils

Fluid	Soil	Level of fluid application %	Average seed germination %
Therminol 66	Soil JF79	0-20.20	98
		4.00	97
		7.96	53
		15.80	1
		24.00	2
	Aiken	0-7.96	98
		15.80	97
		24.00	45
	Yolo	0-4.00	98
		7.96	97
		15.80	23
		24.00	2
	Egbert	0-15.80	98
		24.00	94
Syltherm 800	Soil JF79	0-1.86	98
		3.71	97
		7.43	19
		14.90	4
		22.30	2
	Aiken	0-7.43	98
		14.90	70
		22.30	19
	Yolo	0-3.71	98
		7.43	96
		14.90	44
		22.30	11
	Egbert	0	98
		0.45	73
		0.93	80
		1.86	87
		3.71	89
		7.43	86
		14.90	85
		22.30	87

Table 5

The ratios of the treatment seedling yield (T) to the control seedling yield (C) for four Syltherm-treated soils

Soil	Treatment level %	Average seedling yield g/pot	Ratio T/C
Soil JF79	0	1.34	
	0.45	1.37	1.02
	0.93	1.32	.99
	1.86	1.31	.98
	3.71	1.31	.98
	7.43	0.18	.13
	14.90	*	
	22.30	*	
Aiken	0	1.40	
	0.45	0.97	.69
	0.93	1.11	.79
	1.86	1.12	.80
	3.71	1.20	.86
	7.43	1.20	.86
	14.90	0.71	.51
	22.30	0.10	.07
Yolo	0	1.46	
	0.45	1.27	.87
	0.93	1.36	.97
	1.86	1.28	.88
	3.71	1.33	.91
	7.43	1.25	.86
	14.90	0.50	.34
	22.30	0.05	.03
Egbert	0	1.85	
	0.45	0.71	.38
	0.93	1.12	.61
	1.86	1.21	.65
	3.71	1.07	.58
	7.43	1.16	.63
	14.90	1.07	.58
	22.30	0.98	.53

* Trace amount

Table 6

Average percentage of seed germination at various application levels of Partherm 430 to four soils

Soil	Level of fluid application %	Average seed germination %
Soil JF79	0-0.80	98
	1.20	97
	2.40	5
Aiken	0-1.20	98
	2.40	94
Yolo	0-0.80	98
	1.20	96
	2.40	88
Egbert	0-1.20	98
	2.40	96

Table 7

Chemical analysis of thermal transfer/storage materials

Material	Element*									
	Al	Fe	Mn	Co	Cr	Zn	Cu	Cd	Pb	Ni
	mg/l									
Therminol 66**	2.95 (7.50)	7.42 (2.94)	0.35 (0.26)	ND	0.03 (0.13)	0.46 (0.45)	0.41 (0.09)	0.04 (0.01)	1.69 (0.40)	ND
Caloria HT43**	ND	0.29 (0.49)	0.17 (0.28)	ND	0.69 (0.98)	2.19 (0.34)	0.08 (0.03)	0.02 (0.01)	0.04 (0.16)	0.42 (0.27)
Dow 200**	142.80 (60.10)	10.05 (2.58)	0.82 (0.91)	ND	ND	0.72 (0.07)	0.95 (0.35)	0.16 (0.19)	2.01 (0.85)	0.60 (0.19)
Caloria HT43 (Coolidge)	ND	1.85 (1.71)	0.03 (0.03)	ND	0.08 (0.11)	0.54 (0.59)	0.33 (0.53)	0.01 (0.01)	ND	0.42 (0.78)
Caloria HT43 (Willard)	5.05 (4.60)	2.17 (1.08)	0.10 (0.03)	ND	1.16 (0.48)	2.13 (3.20)	2.39 (0.19)	0.09 (0.02)	0.51 (0.28)	10.78 (3.95)
Therminol 66 (Sandia)	26.05 (30.69)	5.87 (4.02)	0.48 (0.41)	ND	1.45 (0.53)	6.66 (1.80)	5.57 (1.32)	0.25 (0.02)	3.11 (1.86)	6.56 (4.62)
Syltherm 800 (Sandia)	34.70 (10.11)	10.62 (4.96)	0.35 (0.17)	ND	0.82 (0.72)	3.44 (2.18)	1.45 (1.39)	0.12 (0.04)	1.84 (2.00)	2.21 (3.85)
	μg/g									
Partherm 430	0.98 (0.72)	ND	ND	ND	172.80 (28.60)	14.80 (2.10)	0.21 (0.05)	ND	ND	ND

* Mean (standard deviation) of triplicate analysis, except Partherm 430, which was in duplicate.
ND = not detectable

** Fresh oils. These oils were not of the same batch as those used in solar applications.

Table 8

Free fatty acids and organic peroxides in used thermal transfer/storage fluids

Used fluid	Use history	Free fatty acids %*	Peroxides μmole/g oil
Caloria HT43 (Coolidge)	**	ND	0.04
Caloria HT43 (Willard)	**	ND	ND
Therminol 66	**	0.014	0.14
Syltherm 800	**	0.011	ND

* Percent as oleic acid

** See table 1 for use history

Table 9

Effect of heating on the gas chromatographic distribution of components in Caloria HT43

Peak retention time	Area under chromatogram peaks**		
	Treatment A*	Treatment B*	Treatment C*
	picoampere-second per microliter***		
23.37	55.05		
24.37	10.96	2.33	
26.06	11.61	1.39	0.82
29.01	12.88	5.80	18.55
31.73	24.66	2.75	9.24
32.38	82.27	2.93	3.73
34.07	15.48		
79.07	13.78		
96.75	36.91	3.34	
118.59	76.96	13.10	
145.08	106.67	25.77	
175.84	128.85	35.15	
209.80	108.82	32.91	
214.24	56.31		
245.83	83.35	19.25	
286.56	40.07		

* Treatment A: control; treatment B: heated at 80°C, 4 h/d, 5 d/wk for 7 weeks; treatment C: heated at 160°C, 4 h/d, 5 d/wk for 4 weeks.

** Area is determined electronically. It is the integrated signal in terms of picoampere-second (Hewlett-Packard 1979).

*** One microliter of 1 to 20 dilution of oil in pentane.

Table 10

Correlation between retention time and hydrocarbon chain length*

Retention time (min)	Chain length (C no.)
16.38	C_5
23.26	C_6
29.08	C_8
36.42	C_9
44.82	C_{10}
54.00	C_{11}
67.20	C_{12}
99.64	C_{14}
121.03	C_{15}
149.36	C_{16}
178.98	C_{17}
211.60	C_{18}
287.44	C_{20}

* The operating parameters for gas chromatograph was the same as for Caloria HT43 (table 2).

Table 11

Effect of heating on the gas chromatographic distribution of components in Therminol 66

Peak retention time	Area under chromatogram peaks**		
	Treatment A*	Treatment B*	Treatment C*
	picoampere-second per microliter***		
32.53	47.25	48.81	7.98
33.44	194.41	205.56	69.98
34.25	125.09	138.45	34.14
37.94	984.28	1,037.27	436.03
38.41	461.52	487.46	252.13
39.46	619.23	656.43	375.01
40.93	1,178.23	1,254.11	1,071.38
42.23	796.29	851.59	819.89

* Treatment A: control; treatment B: heated at 80°C, 4 h/d, 5 d/wk for 7 weeks; treatment C: heated at 160°C, 4 h/d, 5 d/wk for 4 weeks.

** Area is determined electronically. It is the integrated signal in terms of picoampere-second (Hewlett Packard 1979).

*** One microliter of 1 to 20 dilution of oil in xylene.

Table 12

Free fatty acids and organic peroxides in fresh thermal transfer/storage fluids after heating in an open container

Fresh fluid*	Treatment**	Free fatty acids %	Peroxides μmol/g oil
Therminol 66	A	ND	1.31
	B	ND	20.21
	C	1.31	1.19
Caloria HT43	A	ND	ND
	B	ND	1.91
	C	ND	T

* Fresh fluids are materials as obtained from the manufacturers. They are not of the same batch used in the projects mentioned in table 1.

** A - control (untreated fresh oil); B - heated at 80°C, 4 h/d, 5 d/wk for 7 weeks; C - heated at 160°C, 4 h/d, 5 d/wk for 4 weeks.

ND = not detectable, T = trace.

Table 13

Free fatty acids and organic peroxides in fresh thermal transfer/storage fluids that were exposed to natural elements for extended periods of time

Fresh fluid*	Treatment**	Free fatty acids %	Peroxides µmol/g oil
Therminol 66	A	ND	1.31
	D	3.74	37.11
	E	8.88	28.91
Caloria HT43	A	ND	ND
	D	1.22	0.49
	E	3.40	T
Dow 200	A	ND	ND
	D	ND	T
	E	ND	0.5

* Fresh fluids are materials as obtained from the manufacturers. They are not of the same batch used in the projects mentioned in table 1.

** A - control (untreated fresh oil); D - continuously exposed to natural elements for 1 month (daily cycle of solar radiation and darkness, ambient air and temperature); E - continuously exposed to natural elements for 2 months.

ND = not detectible, T = trace.

Table 14

Approximate plant toxicity threshold level of various thermal transfer/storage materials in four different soils

	Approximate toxicity threshold level*			
Material	Soil JF79	Aiken	Yolo	Egbert
	percent			
Caloria HT43 (Coolidge)	3.37	13.50	6.74	>20.20
Caloria HT43 (Willard)	3.40	13.60	6.80	20.40
Therminol 66	4.00	7.96	4.00	0.49
Syltherm 800	3.71	0.45	0.45	<0.45
Partherm 430	1.20	1.20	1.20	1.20
Toluene	8.00	0.50	4.00	0.50

* Level above which significant decrease of barley seed germination and/or seedling yield occurred.

Table 15

Electrical conductivity of saturation paste extracts of soils treated with various amounts of Partherm 430

Amount of Partherm 430 applied %*	Electrical conductivity (mmho/cm) of soil			
	Soil JF79	Aiken	Yolo	Egbert
0 (control)	0.32	0.71	0.73	10.77
0.05	3.02	1.95	1.93	10.90
0.10	6.02	3.17	3.20	12.17
0.20	10.59	5.40	5.42	13.13
0.40	19.07	9.62	9.60	15.57
0.80	36.03	17.23	17.80	19.05
1.20	49.97	23.23	24.50	23.80
2.40	87.23	42.57	45.97	34.50

* Percent by weight.

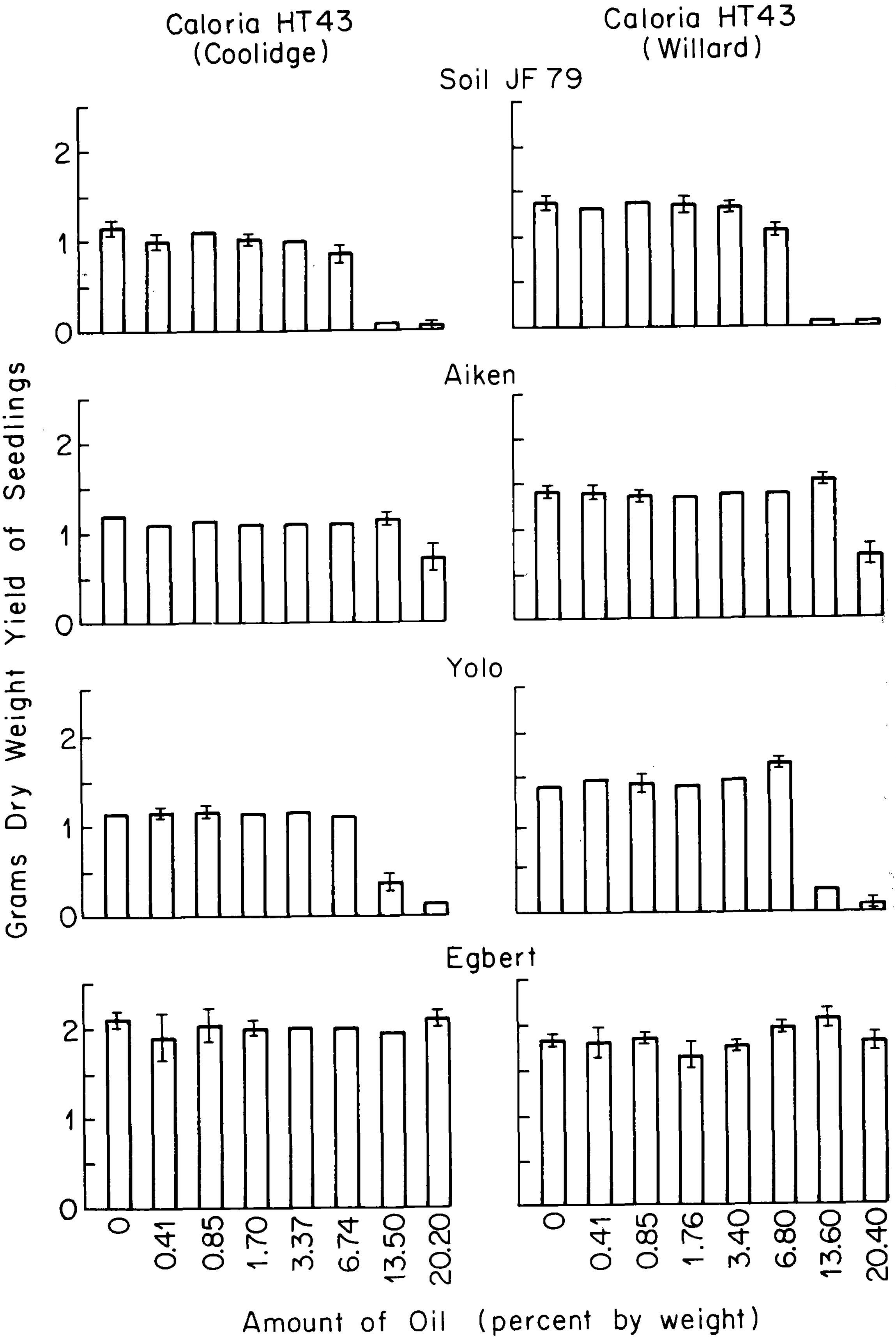

Fig. 1. Barley seedling yields in four different soils contaminated with various amounts of used Caloria HT43 (Coolidge) and Caloria HT43 (Willard). (The "I" sign on the bars indicates the standard deviation of the treatments in triplicate. When <0.05 g, they are not shown.)

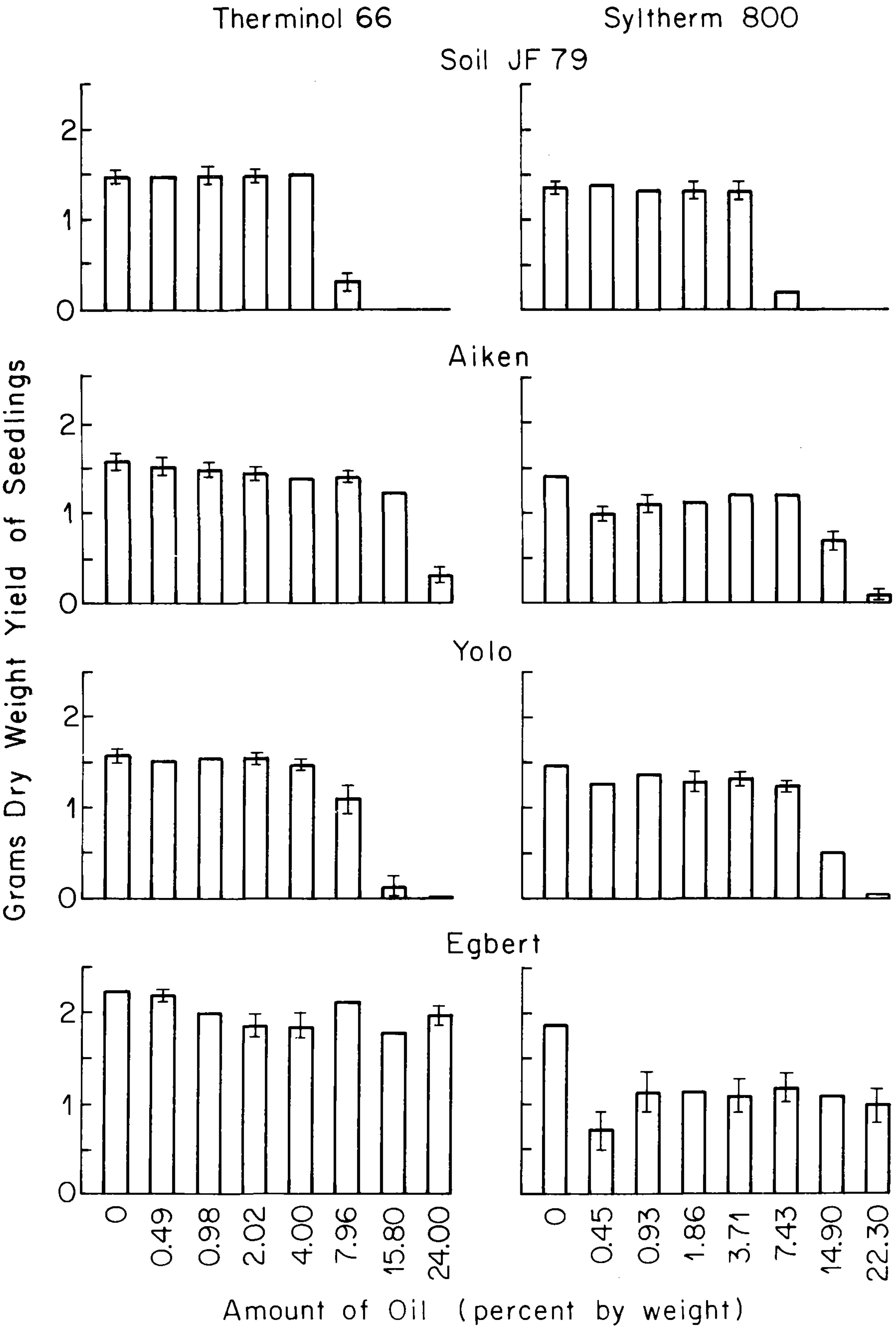

Fig. 2. Barley seedling yields in four different soils contaminated with various amounts of used Therminol 66 and Syltherm 800. (The "I" sign on the bars indicates the standard deviation of the treatments in triplicate. When <0.05 g, they are not shown.)

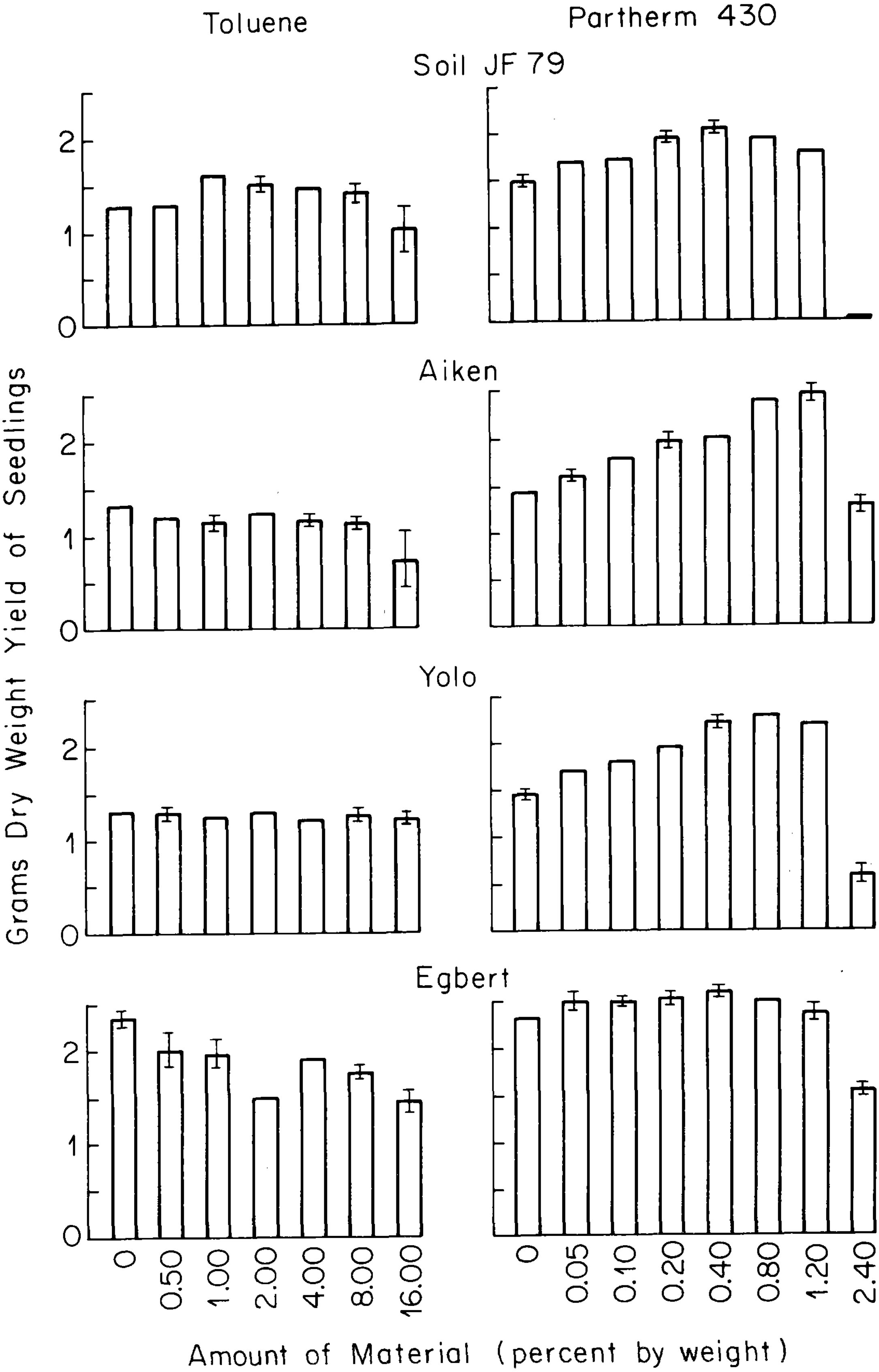

Fig. 3. Barley seedling yields in four different soils contaminated with various amounts of fresh toluene and used Partherm 430. (The "I" sign on the bars indicates the standard deviations of the treatments in triplicate. When <0.05 g, they are not shown.)

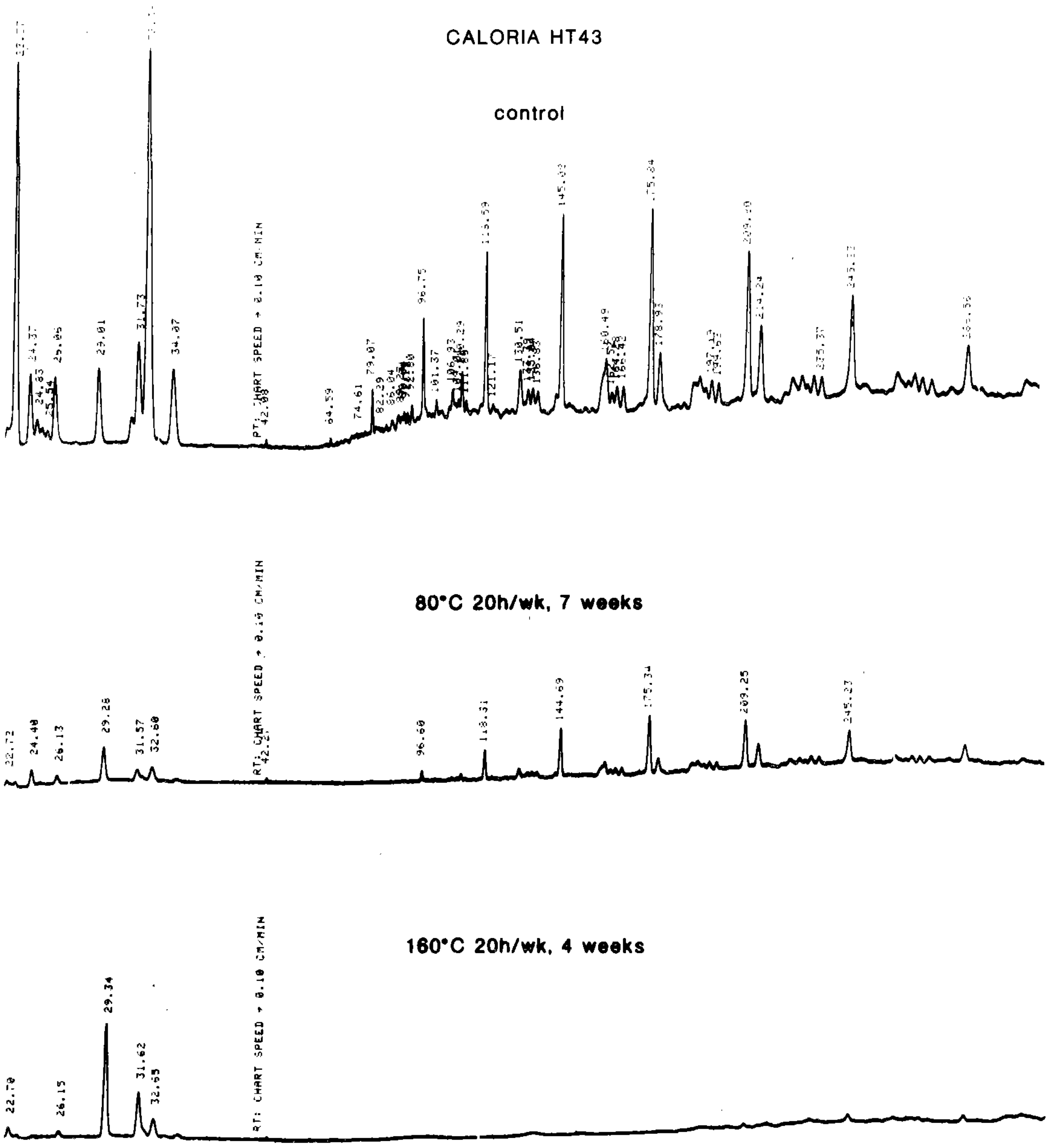

Fig. 4. Gas chromatograms of Caloria HT43 after several treatments (control; 80°C 20 h/wk, 7 weeks; 160°C 20 h/wk, 4 weeks).

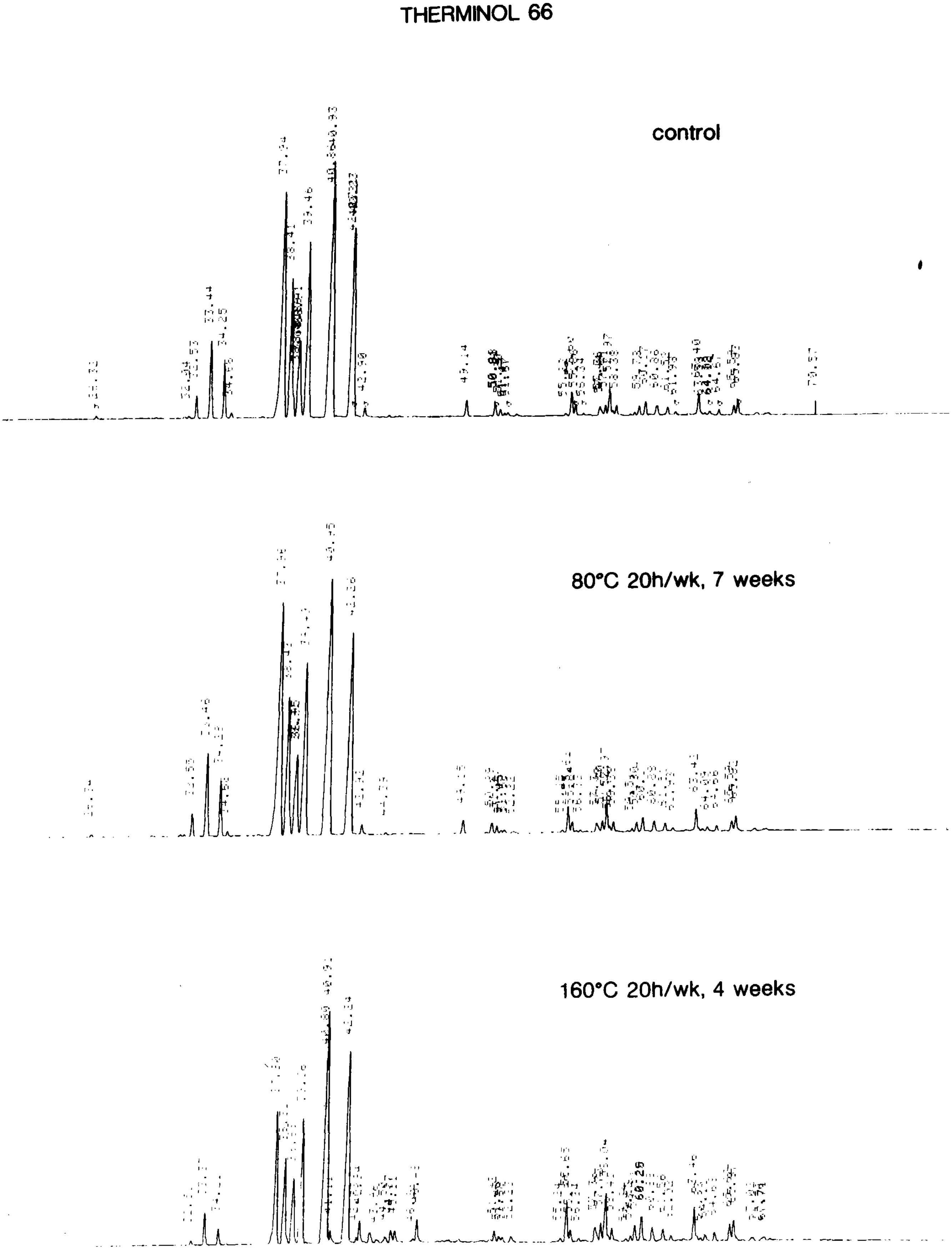

Fig. 5. Gas chromatograms of Therminol 66 after several treatments (control, 80°C 20 h/wk, 7 weeks; 160°C 20 h/wk, 4 weeks).