The action and durability of cetyl alcohol as an evaporation suppressant in soils [1]

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Summary

Analysis of data on the rise of temperature ahead of the wetting front in four soils treated with cetyl alcohol and untreated soils indicated that the effect of treatment on the water-conducting characteristics resulted from induced hydrophobicity of the soil particles. The expected effect of treatment on infiltration and evaporation can be inferred from the soil-water diffusivity relationship of the treated and untreated soil. Treatment with cetyl alcohol had little effect on the passage of water vapour through the soil. Cetyl alcohol was moved to a limited extent by the wetting front because of its presence at the air-water interface. The presence of cetyl alcohol at the wetting front, however, appeared to have little effect on the water movement through the soil.

After 30 weeks in the field the amount of hexadecanol that could be extracted from the soil was less thans 7 % of the amount originally present.

From the results conclusions were drawn regarding criteria for evaporation suppressants and measurements that can be used to test for these.

Introduction

The application of fatty alcohols in reducing evaporation loss from open water surfaces has prompted investigations of the possible role of fatty alcohols in suppressing evaporation from soils. The effectiveness of the evaporation reduction was usually found to be greater on sand than on loams and other finely textured soils (Law, 1964). The mechanism by which the fatty alcohol suppressed evaporation from the sand was assumed to be the same as that which acts to reduce evaporation from an open water surface, i.e. by forming monomolecular films of the alcohol molecules on the water surfaces, oriented with their hydrocarbon tails away from the water surface. The mechanism by which the fatty alcohol suppressed evaporation from finely textured soils was assumed to be by reducing capillary flow of water to the soil surface and thus causing the formation of a dry diffusion barrier (Law, 1964; Olsen et al., 1964).

In an earlier study on different evaporation suppressants (Kijne, 1968) it was suggested that generally the hydrophilicity of the soil governs the water movement in soil, but that after treatment with cetyl alcohol two mechanisms are operative in reducing

water movement. The first results from the hydrophobic coating of the particles and the second from a film of fatty alcohol molecules at the advancing air-water interface. The present study was initiated to investigate further the action of cetyl alcohol and to find out whether water vapour movement was reduced by treatment of the soil or whether the effect on evaporation was entirely due to coating of the soil particles. In addition, it was studied whether cetyl alcohol moved in the soil with the wetting front, as might be expected when cetyl alcohol forms a surface film on the advancing water surface. To this end the penetration of water into columns of treated and untreated soil, and the temperature fluctuations associated with the penetration of the wetting front were measured, and the rate of breakdown and the movement of cetyl alcohol was studied under field conditions.

It was hoped to gain an understanding of the action of this particular evaporation suppressant in order to formulate some criteria for chemical evaporation suppressants in general.

Experimental procedures

The soils used were a fine sandy loam (Urrbrae red brown earth, A horizon, taken from wheat-fallow rotation plots), a clay loam (the B horizon of the same soil), a loamy sand (solodized solonetz), and a friable clay soil (black earth).

The treatment with cetyl alcohol consisted of mixing air-dried soil and a 1 % solution of cetyl alcohol (commercial mixture of 52 % n-hexadecanol 42 % n-octa-decanol, and 6 % n-tetradecanol) in ethyl-alcohol, in a ratio of 100 g soil and 25 ml solution.

The temperature fluctuations at the wetting front were monitored with a 50.000 Ω thermistor in a Wheatstone bridge circuit, and recorded on a millivolt recorder. In thais manner temperature variations of $\pm$ 0.005° C could easily be detected. The temperature was recorded during horizontal infiltration of a 0.005 M CaSO$_4$ solution in distilled water into soils which were packed in clear acrylic plastic cylinders. The liquid entered the soil columns through a fritted glass bead plate (see Fig. 1). The plate was filled with the permeating liquid and a suction of 2 cm was maintained in the liquid source by the use of a Mariotte bottle. The liquid source and soil column
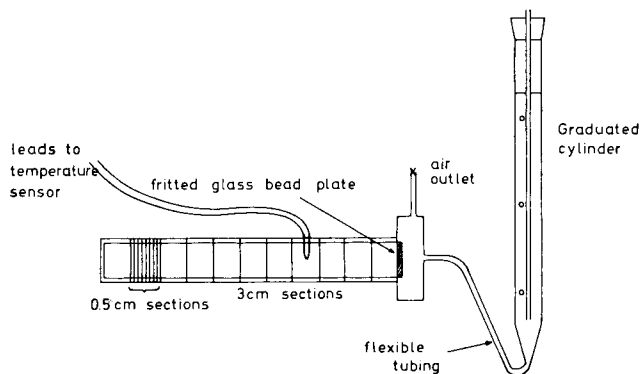

Fig. 1. Experimental apparatus used for horizontal water movement.

were placed in a constant temperature air bath maintained at $\pm$ 0.01° C. The opening of the taps which initiated the flow into the soil columns, was manipulated from outside the constant temperature bath. The advance of the wetting front could be seen through a plexiglass window in the styrofoam air bath. The temperature sensor was placed at either 4.5 or 10.5 cm from the liquid source. During some runs the actual passing of the wetting front was recorded when the wetting front short-circuited the thermistor by closing a contact (0.2 mm wide) located 1.0 mm from the thermistor and in the same plane. This contact was wired in parallel with the thermistor in the same bridge circuit. The parallel shunt could be opened again by a switch.

The durability of cetyl alcohol treatment of the Urrbrae A soil was determined under field conditions in Australia. Eight acrylic plastic containers, 7 cm ϕ and 13 cm high, were placed in shallow tight-fitting holes so that the top of the container was level with the surface of the surrounding fallow soil. The lower halves of the containers were filled with untreated soil and the top with cetyl alcohol treated Urrbrae soil. After 5, 10, 18 and 30 weeks two of the containers were taken from the field and the soil was analysed for the presence of hexadecanol. The soil of both top and bottom half was sectioned and dried overnight at 65° C. The hexadecanol was extracted by shaking 5 g of the oven-dried soil with 10 ml ethyl-alcohol for 10 min. Of the filtered extract 4 μl was then analysed in a gas chromatograph (Perkin-Elmer, No 801). The recorded traces were compared with those obtained from extracts of the treated soil kept air dry in the laboratory, and with a 1 % solution of cetyl alcohol in benzene.

Results

The temperature rise associated with the wetting-front infiltrating into untreated soils and soils treated with cetyl alcohol is given in Table 1. The values are averages of 4-6 runs. There was no systematic difference in the total temperature rise observed with the thermistor at 4.5 and at 10 cm from the liquid some. The rate of rise, however, was slower in the case with the thermistor at a greater distance from the source. A characteristic curve is presented in Fig. 2. The maximum temperature was found to be associated with the actual passing of the wetting front which caused momentary short-circuiting of the temperature sensor. As can be seen in Fig. 2 the temperature dropped

Table 1. Temperature rise associated with a wetting front infiltrating into untreated soils and soils treated with cetyl alcohol.

Soil	Treatment	Temperature rise (° C)
Urrbrae A	Untreated	0.20
	cetyl alcohol	0.01
Urrbrae B	Untreated	0.55
	cetyl alcohol	0.05
Solodized solonetz	Untreated	0.30
	cetyl alcohol	0.30
Black earth	Untreated	0.60
	cetyl alcohol	0.25

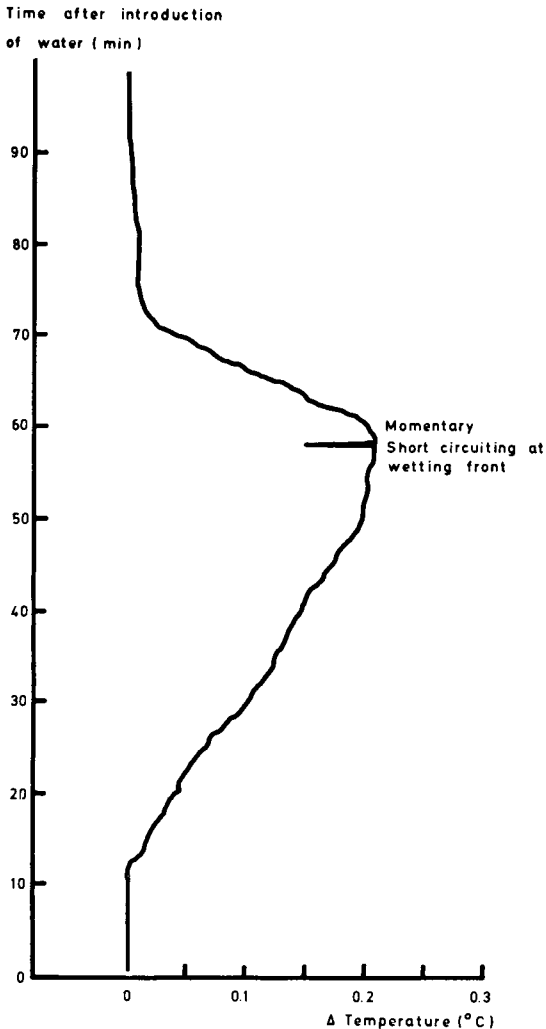Time after introduction
of water (min)

Fig. 2. Characteristic temperature fluc-
tuation associated with the wetting front
infiltrating into an Urrbrae A soil, with
the thermistor at 4.5 cm from the liquid
source.

again to the same or nearly the same level as before the wetting front had passed. This drop in temperature was usually somewhat erratic and not quite as reproducible as the temperature rise.

The durability of the cetyl alcohol treatment of Urrbrae A soil under field conditions in South Australia is expressed in Fig. 3. The height of the hexadecanol peak traced on the recorder of the gas chromatograph is plotted as a fraction of the peak height given by the concentration of hexadecanol in the reference soil as a function of the time that the soil samples were in the field. The data in Fig. 2 are averages of three extracts of 5 g samples taken from the same depth in the two containers. The variability between duplicates was at most 8 %.
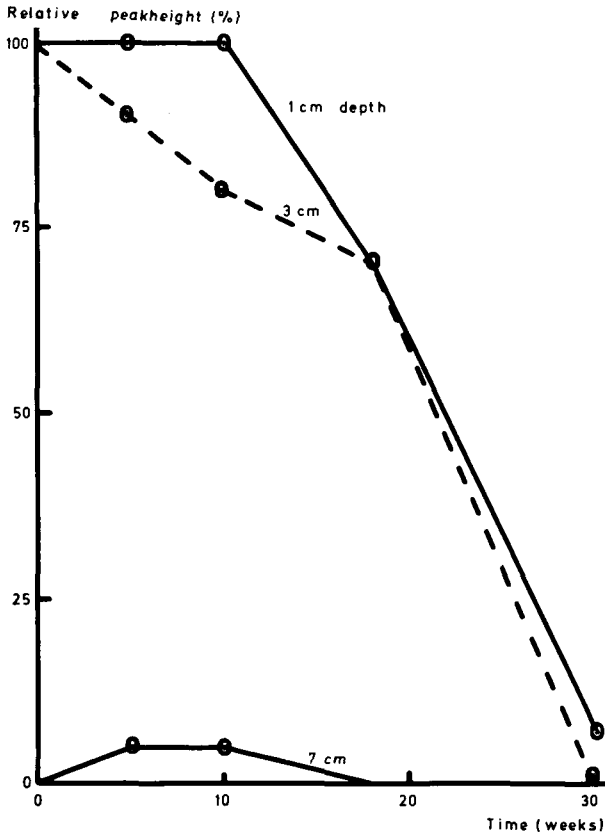
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Fig. 3. Relative peakheight of the GLC peak of hexadecanol as a function of time in the field, extracted from the soil at 1, 3 and 7 cm depth.

Discussion

Influence of treatment on evaporation

Treatment with cetyl alcohol influenced evaporative losses from soils as was reported earlier (Kijne, 1968, 1971). From these earlier studies it appeared that this influence is rather complicated since both evaporation and infiltration are affected. Higher moisture contents are found at shallow depth in those treated soils of which the infiltration rate is reduced by treatment with cetyl alcohol. Although in these treated soils more water is located near the evaporative surface, the cumulative evaporation from treated soil was found to be less than from untreated soil for a certain period of time. Thereafter the cumulative evaporation of water from a treated soil often surpassed that from the untreated soil. The duration of the period of lower cumulative evaporation depended on the relative magnitude of the effect on infiltration and evaporation; this was only 2 or 3 days in the heavy black soil, and about 3 weeks for the Urrbrae A soil.

Influence on the temperature rise

In three of the four soils investigated the cetyl alcohol treatment greatly reduced the temperature rise associated with a wetting front infiltrating into the soil (Table 1). The exception is the solodized solonetz; this, however, does not mean that cetyl alcohol was not adsorbed on this soil because gas chromatographic analysis of the soil extract indicated the presence of hexadecanol.

The observed temperature variations at the wetting front are of the same order as those reported by Anderson et al. (1963) for an air-dried sandy loam soil. These authors suggested that the heat arises from the condensation of water vapour that precedes the arrival of the wetting front. As the vapour condenses the latent heat of vapourization is released. The reduction in temperature rise as a result of treatment is due to a coating of cetyl alcohol over the particles. The cetyl alcohol molecules are probably adsorbed by clay particles by ion-dipole interactions and Van der Waals forces. The molecules are oriented with their hydrocarbon tails perpendicular to the mineral surfaces, and the hydrophobic character of the alcohol molecules increases with the size of the alkyl group. The temperature rise is then an approximate relative measure of the difference in surface energies of wetted surfaces and those in equilibrium with the ambient vapour pressure. If the liquid wets the solid well the energy change is large, and for a contact angle of 90° the energy change is zero. The results then lend further credit to the suggestion made before that the reduction in evaporation due to treatment with cetyl alcohol is, at least in part, the result of hydrophobic coating of the particles.

Influence on the rate of vapour movement

In some instances, the rate of vapour movement was calculated from the rise in temperature of two temperature sensors which were placed at different locations in the soil column. The rate of vapour movement was not consistently affected by treatment and it is likely that the variations obtained resulted from the uncertainty involved in determining accurately the initiation of the temperature rise which indicated the arrival of vapour at the sensor site. This is consistent with the view expressed by Gardner and Hanks (1966) that treatment with cetyl alcohol had no net effect on the passage of water vapour through the treated soil.

This then implies that the observed effect of treatment on evaporation is due to an effect on the movement of water as liquid through the soil.

Influence on the soil-water diffusivity

Here we need to turn to a discussion on the influence of cetyl alcahol treatment on the soil-water diffusivity relationship, because the results discussed sofar are entirely consistent with the observed effect of treatment on the diffusivity. The technique and some of the early results have been discussed before (Kijne, 1968).

The diffusivity, D, as function of moisture content, ϑ, is presented in Fig. 4, for the treated and untreated Urrbrae B and solodized solonetz soils. The influence of cetyl alcohol treatment on the unsaturated water movement, as exemplified by the $D(\vartheta)$ relation, was less marked for the solodized solonetz than for the other soils. The relationship for the black earth is similar to the one for the Urrbrae B. The diffusivity for treated und untreated Urrbrae A was presented before (Kijne, 1968). It can be
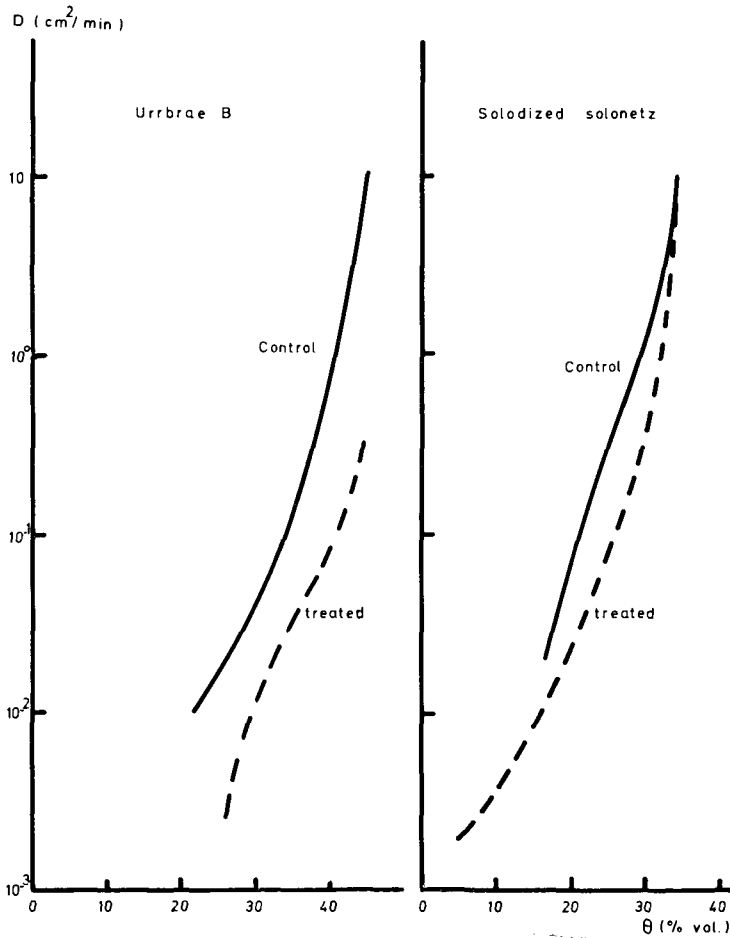
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Fig. 4. Soil-water diffusivity versus volumetric water content for treated and untreated Urrbae B and solodized solonetz soils.

seen in Fig. 4 that the diffusivity of all soils was reduced for water contents near saturation, except of the solodized solonetz. A reduced infiltration rate into the soil is reflected in a reduction in diffusivity values near saturation (cf. Hanks and Bowers, 1963, and DeBano, 1971), and hence these results imply that the infiltration rate of water into the solodized solonetz was not affected by the cetyl alcohol treatment, whereas those of the other soils were reduced. This observation was borne out by infiltration experiments in the field (unpublished data by the author).

At values of the soil moisture content below saturation the diffusivity of all soils, including the solodized solonetz, was affected. It is likely that in a soil in which some of the particle surfaces are coated with a hydrophobic substance the liquid-solid interfaces should possess large wetting angles, but numerous wettable sites are probably still available for water adsorption. DeBano (1971) suggested that after water has been

absorbed on hydrophobic soils some of the interfaces may coalesce and form a some-what continuous layer of water having fewer interfaces to hinder liquid flow. There-fore as water content increases the difference in diffusvity between treated and un-treated soil should diminish. This effect, which was also noted for the Urrbrae A soil, although to a lesser extent (Kijne, 1968), probably explains the curves for the solodized solonetz in Fig. 4. The Urrbrae B and the black earth, which have considerably larger specific surface areas, do not show this effect. Thus, the expected effect of cetyl alcohol treatment on reducing evaporation from bare soil can be inferred from an analysis of the $D(\vartheta)$ curves of treated and untreated soils. Lower $D(\vartheta)$ values for treated soils at those soil moisture contents that occur at the soil surface imply reduced evaporation; this effect will be more marked and longer lived when the diffusivity near saturation is not affected by treatment.

The durability of cetyl alcohol in the soil

The results on the durability of the cetyl alcohol treatment of Urrbrae A soil under field conditions are summarized in Fig. 3. A significant amount of hexadecanol was extracted at a depth of 7 cm in soil which was untreated at the start of the experiment. This indicates that cetyl alcohol was moved with the wetting front. Hence not all cetyl alcohol was adsorbed on the soil particles. After 30 weeks very little hexadecanol could be extracted. The reduction in the octadecanol content, which was originally present as component of the commercial cetyl alcohol, was similar to the decrease in hexadecanol, but after 30 weeks the relative peak height of the octadecanol was still about 20 %. The breakdown of cetyl alcohol in soils is most likely bacterial and it is surprising in view of the decomposition of hexadecanol films on surface waters (Chang et al., 1962) that the extractable hexadecanol content did not decrease even faster. Movement of hexadecanol with the wetting front was also observed by Myhr-man and Evans (1969) who used ^{14}C-tagged hexadecanol. They presumed that move-ment took place in the form of small buoyant particles. A period of 10 weeks of stability of hexadecanol in the soil observed by Myhrman and Evans (1969) is in good agreement with data from our study presented in Fig. 3.

The question now arises whether the presence of a cetyl alcohol film at the advan-cing air-water interface by itself has any influence on the passage of water through the soil. It is difficult, if not impossible, to separate the effect of this film from the effect of the induced hydrophobicity of the particles. It is likely that, if one attempted to measure the rate of movement of a wetting front at which a cetyl alcohol film is present through an untreated soil, the film soon would be disrupted because of pre-ferential adsorption of the cetyl alcohol by the soil particles. It may be speculated that the presence of a monomolucular film at the advancing air-water interface is not essen-tial for the effectiveness of evaporation suppressants. It can then be concluded that the effectiveness of cetyl alcohol as an evaporation suppressant of water from soils is due to an effect of treatment on the surface properties of the soil particles, which causes a lowering of the diffusivity at the intermediate soil moisture contents. In most soils, however, the induced hydrophobicity of the particles has also the effect of reducing the infiltration rate of water into the soil. A corollary to this conclusion is that the search for effective evaporation suppressants should aim at materials that are non-toxic to plant growth, and induce hydrophobicity of soil particles that is particularly evident at water contents sufficiently below saturation that the infiltration capacity of the soil is not impaired.

The techniques mentioned in this paper, i.e. measurements of soil-water diffusivity and the temperature rise associated with the penetration of a wetting front in untreated and treated soil, seem particularly siuted for testing possible evaporation suppressants.

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