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POTASSIUM RELEASE IN SOILS AS AFFECTED
BY DRYING

by

Thomas Edward Bates

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INTRODUCTION

Soils contain large amounts of K, but as most of it is not readily available to plants large quantities of K fertilizers are added annually. In order to determine the optimum application of fertilizer, it is important that the availability of the soil K to plants should be measured accurately.

Potassium extracted from the soil with neutral, 1N NH_4Ac , usually called exchangeable K, is very commonly used as a measure of available K.

Many soils of the North Central region of the U.S.A. release K on drying. That is, the exchangeable K values that are obtained from dried samples are higher than those obtained from the original field-moist samples. Also, when dried samples of these soils are re-wet with water some of the K becomes non-exchangeable, but the exchangeable K values do not decrease to the initial level found in the moist soil. For this reason there has been some uncertainty as to the significance of these different exchangeable K values. It is now known that for some soils the exchangeable K extracted from air-dried or oven-dried samples does not correlate as well with K uptake by plants as the exchangeable K extracted from undried samples.

Soil testing laboratories usually determine exchangeable K by extraction of air-dried samples in spite of the resulting lower correlation with K uptake by plants. This is done

because several practical problems would be encountered if moist soils were used. Farmers probably would not be sufficiently careful to prevent drying during sampling, thus some samples would be dry when they reached the laboratory and some would be moist. Packaging of moist samples for delivery to the laboratory would cost slightly more. In the laboratory, moist samples would be difficult to mix and sub-sample. Moisture determinations would also be required to correct exchangeable K values to a constant moisture basis.

Although many soils release K to the exchangeable form when dried, some soils fix K, or convert it from the exchangeable form to a non-exchangeable form, on drying. Most of the soils which normally release K on drying, will fix considerable amounts if sufficient quantities are added. Page and Baver (1940) suggested that K ions were fixed as a result of being trapped in the cavities formed by adjacent hexagonal O rings in a 2:1 type clay mineral. The charge on the K ions is believed to pull the lattice layers together, forcing out the water of hydration. Drying of the soil or mineral is believed to make the lattice easier to collapse by removing some of the interlayer water and thus increased fixation results. This theory is widely accepted and appears to offer a logical explanation of fixation on drying. Release of K on drying, however, cannot be explained on this basis and no adequate theory has been presented to explain it. Consider-

able work has been done to determine the amount of release that occurs in different soils and efforts have been made to study factors which affect release. Little progress appears to have been made in understanding the phenomenon, however.

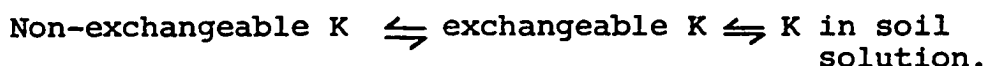
The main objective of these investigations was to discover factors which affect release of K on drying and to study these factors in an effort to develop a reasonable explanation of how and why release occurs when soils are dried. A second objective was to find a method of drying a soil without changing the exchangeable K value, and to find a method of treating a dried soil so that the exchangeable K extracted would be the same as from an undried soil.

In this manuscript the term "release" unless otherwise specified, will be used to designate the increase in exchangeable K that occurs when soils are dried. "Reversion" will be used to designate the fixation of that K which has been released on drying.

LITERATURE REVIEW

The literature on K in soils and plant nutrition is quite extensive. Several good reviews are available, however, that of Reitemeier (1951) being one of the most comprehensive. More recent reviews on K fixation have been written by Hanway (1954), Welch (1958), Schuffelen and van der Marel (1955), Edwards (1960), and Agarwal (1960).

Peech and Bradfield (1943) divided soil K into three forms which they considered to be in equilibrium as indicated in the expression:



These relationships are now generally accepted. The conversion of applied K from the water soluble or exchangeable to the non-exchangeable state is usually termed "fixation", while the conversion of non-exchangeable K to the exchangeable or water soluble state is termed "release".

Plant Uptake and Chemical Extraction of Potassium
from Moist Soils and Minerals

Reitemeier (1951) states that high potash micas and feldspars invariably liberate some K to plants and extractants. Blanck (1912,1913) and Plummer (1918) showed that availability to plants of K from minerals decreased in the order: biotite > muscovite > orthoclase > microcline. Gorbunov (1940) ex-

plained the greater ease of extraction of K from mica over that from orthoclase on the basis of type of atomic bonding and crystal structure. In micas the cleavage plane between layers is the site of K ions which can be removed by cation exchange. In orthoclase the occurrence of co-valent bonds and the location of potassium inside the crystal lattice hinder its extraction. Barshad (1948) was able to transform biotite into vermiculite by treatment with Mg solutions at 70° C. and to transform vermiculite to biotite by similar treatment with K solutions. Caillière et al. (1949) were able to expand the lattice of muscovite and illite by boiling in concentrated CaCl_2 solutions. Hydration of mica particles by weathering is shown by Barshad (1950) to be due chiefly to the replacement of interlayer K by Ca, Mg and H. Walker (1949) observed a natural transformation of biotite to vermiculite within a soil profile.

It has been observed for many years that the exchangeable and water soluble K in unfertilized soils are insufficient to account for that removed by repeated cropping. The amount of non-exchangeable K taken up by plants has in some cases been considerable. Bear et al. (1944) found a maximum uptake of 235 pounds K_2O per acre in 12 months, Reitemeier et al. (1948) up to 740 pounds in 740 days and Ayres (1949) obtained values up to 1256 pounds in 42 months.

Bray and DeTurk (1939) concluded from their work that the

extractable K in soils would increase when the exchangeable K content was below the equilibrium level. Thus moist storage of field samples at equilibrium resulted in no change but moist storage of samples leached with HCl increased the exchangeable K to the equilibrium level. Ayres (1949) found that moist storage of Hawaiian soils for 42 months did not change the exchangeable K levels, but removal of part or all of the exchangeable K before storage resulted in small or large increases, respectively. The average amount of K taken up during cropping was approximately 8 times as great as the increase in exchangeable K in the same soils stored moist while H saturated.

Olsen and Shaw (1943) working with the silt fractions of three Ohio soils found that uptake of non-exchangeable K in Neubauer tests increased with decreasing particle size. Merwin (1950) showed with four New York soils that the clay fraction accounted for 40 to 83 percent of the increase in exchangeable K compared to 15 to 51 percent from the silt fraction and lesser amounts from the sand. From studies of six size fractions of Iowa soils, Pratt (1952) found that HNO_3 extractable K as a percentage of the total K was highest in the less than 0.2 micron fraction of 12 soils out of 13 studied. The amount of HNO_3 extractable K was highest, however, in the 0.2 to 2 micron fraction.

Cation Fixation

Page and Baver (1940) suggested that cations were fixed as a result of being trapped in the cavities formed by adjacent hexagonal O rings of the Si sheets in a 2:1 type clay mineral. Cations with radii approximately the same as those of the cavities could become embedded and their charge, acting on both sheets, would collapse the lattice and prevent extraction. Page and Baver found that K, NH_4 , Rb, Cs and Ba ions, having effective radii similar to those of the hexagonal O cavities, were fixed by Wyoming bentonite. This explanation of the mechanism of cation fixation is now widely accepted.

By removing K from biotite, a contracted lattice mineral, Barshad (1954) has produced vermiculite, an expanded lattice mineral, strongly suggesting that it is the large amount of non-exchangeable K in biotite which prevents expansion of the lattice. He concluded that the magnitude of the interlayer charge, rather than the origin of the charge, determines the extent to which a clay mineral will fix K. Wear and White (1951), on the other hand, found a direct positive correlation between the amount of K fixed and the proportion of the net negative charge originating in the tetrahedral position. It would seem logical that the density and the location of the charge should both be important in determining the ease of replacement of interlayer cations.

The classification of K as exchangeable or non-exchangeable is rather arbitrary. For a given soil or clay mineral capable of fixing K, the amount exchanged, and thus also the amount classed as fixed, varies with the replacing cation, the concentration of replacing cation (Merwin and Peech, 1951), and the temperature or method of extraction (Barshad, 1951). The latter author showed that cations normally considered as fixed could be replaced by Li, Na, Mg, Ca, and Ba ions which were capable of expanding the lattice, but could not be replaced by K, NH_4 , Rb and Cs ions which were unable to expand the lattice. Hanway et al. (1957b) have shown that even low concentrations of fixable cations in the extracting solution can prevent the release of fixed K or NH_4 .

Fixed K is now rather commonly defined as added K that is not extractable with neutral NH_4Ac . Schuffelen and van der Marel (1955) suggested that $\text{Mg}(\text{Ac})_2$ or NaCl were preferable to NH_4Ac as extractants. Since Na is not a fixable cation, it would be expected to extract much more K than NH_4 . Barshad (1951) found Na so much more efficient than K in extracting NH_4 in distillations that he suggested NH_4 fixation be defined as the difference between the amount extracted with Na and that extracted with K. Barium is considered by some authors to be a non-fixable ion (Joffe and Levine, 1947; Martin et al., 1946; Wear and White, 1951), but was found by Page and Baver (1940) to be fixed. Ammonium has been con-

sistently classed as a fixable ion and has been shown to be fixed by soils in similar amounts to K (Joffe and Levine, 1947; Stanford and Pierre, 1947). This coupled with its convenience for use on the flame photometer has made it an appropriate ion for determination of exchangeable K.

Minerals That Fix Potassium

Potassium and NH_4 can be fixed in appreciable quantities by vermiculite (Gruner, 1939; Barshad, 1948; Walker, 1949; Hanway et al., 1957b; DeMumbrum and Hoover, 1958), in somewhat lesser amounts by illites (DeMumbrum and Hoover, 1958; Edwards, 1960) and montmorillonite (Page and Baver, 1940; Stanford and Pierre, 1947; Wear and White, 1951). Stanford (1948) found that fixation by illite increased on drying and fixation by montmorillonite did not occur without drying. Kaolinite is usually not considered as a fixing mineral, although Hoover (1945) reported that small amounts of K were fixed by this mineral.

Exchangeable Soil Potassium as Affected by Changes in Moisture Content

It has been known for many years that changes in soil moisture content affect the form of plant nutrients in soils. Gustafson (1922) presented a long literature review on the effect of drying on the water soluble constituents of soils.

Steenkamp (1928) showed that drying increased the exchangeable bases, including K, in several soils.

In more recent studies Attoe (1947) showed that moist storage of fertilized soils resulted in K fixation which was increased on air drying. Drying of unfertilized soils resulted in K release. He showed further (Attoe, 1949) that the release of K on drying resulted in an increase in the K content of oats that were subsequently grown on these soils. Similar results were presented by Walsh and Cullinan (1951). Seatz and Winters (1944), Reitemeier et al. (1948) and Luebs et al. (1956) present evidence for release of K from soils on air drying. Luebs et al. (1956) plotted soil moisture against exchangeable K for several Iowa soils and showed that the release with loss of water was greater at lower moisture levels. Scott et al. (1957) showed that K was released on drying in soils to which no K had been added, but was fixed on drying in soils to which large amounts of K had been added. Where intermediate rates of K were added, fixation occurred with loss of water at high moisture levels, but release occurred with loss of water at low moisture levels.

Hanway and Scott (1957a) and Hanway et al. (1960) studied the distribution of exchangeable K in the profiles of a number of Iowa soils. The undried subsoils contained smaller amounts of exchangeable K, but in general they released more on air or oven drying than the surface horizons. After drying, the

soils were re-wet and stored moist for various periods of time to study the amount of reversion (fixation of the K which had been released on drying). There was more reversion in samples from lower horizons and from soils with less profile development, indicating that greater reversion occurs in less weathered material. No relation was found between the amount of K released on drying and that which reverted on re-wetting. In all of the soils studied the exchangeable K was lower in the original undried soil than after drying and re-wetting. Hanway et al. (1961), reporting on studies with soils of the North Central Region of the U.S.A., stated that drying of surface soils resulted in increases, no change, or decreases in exchangeable K. Drying subsoils resulted in increases in exchangeable K in all but some sandy soils. Changes in exchangeable K due to drying tended to be smaller in soils from the eastern part of the region and exchangeable K in field moist soils was almost always considerably lower in the subsoil than in the surface.

The Relation of Exchangeable Potassium to Uptake by Plants

Most soil testing laboratories use exchangeable K as a basis for estimating fertilizer requirements. From the discussion just presented, it is apparent that different values are obtained if the K is extracted from field moist, air-dried

or oven-dried soil. It is therefore important that the degree of drying before extraction be chosen to give the best possible correlation of exchangeable K with K uptake and plant growth. Jones et al. (1961) conducted field experiments with corn on five Ohio soil series and found that exchangeable K extracted from air-dry soil was more closely correlated with dry matter yield or K uptake than the exchangeable K extracted from field moist or oven-dry soil. Mathews and Sherrell (1960) in field experiments on 16 Ontario soil types correlated exchangeable K with yield response due to K fertilization. No appreciable differences were found between the coefficients of correlation for the relation between yield response and exchangeable K extracted from moist, air-dry or oven-dry soils. They concluded that exchangeable K extracted from moist, air-dry or oven-dry soils did not account for a satisfactory portion of the variability in yields of wheat, oats and corn. In studies with potatoes the yield response was closely correlated with exchangeable K, particularly exchangeable K extracted from oven-dry soils. Working with 13 Iowa soils, Luebs et al. (1956) correlated K uptake by corn grown on undried soils in the greenhouse with exchangeable K extracted from moist and air-dry samples. He found higher correlation coefficients using the exchangeable K extracted from moist samples. Hanway et al. (1961) reported on field studies with alfalfa on soils of the North Central region of

the U.S.A., Ontario and Alaska. They state that regardless of the index of K response used or the depth of soil sampled to estimate K availability, the index of K response was more highly correlated with K extracted from field-moist than from air- or oven-dried samples. Greenhouse studies with millet on soils of the North Central Region (Barber et al., 1961) show that K uptake correlates better with moist than with air- or oven-dry exchangeable K. It may be concluded from these studies that for soils of Iowa, and at least some other parts of the North Central Region, exchangeable K extracted from the moist soils should be used for soil testing purposes. At the present time, however, most soil testing laboratories are using exchangeable K extracted from air-dry soils due to the inconvenience of handling moist samples.

Postulated Mechanisms of Potassium Release on Drying

Fixation of K by soils on drying can be explained by the accepted theories for moist fixation. Potassium fixation has been shown to be accompanied by expulsion of some of the interlayer water and collapse of the lattice. When a soil is dried, some of the interlayer water is removed. Thus, more K should be fixed on drying than in the moist state. There does not appear to be any such simple explanation of the release of K which occurs on drying. The mechanism suggested for fixation would in fact be expected to prevent release on drying.

Aleksandrov (1950) suggests that release on drying and fixation on re-wetting are caused by bacterial action. This hypothesis ignores the large body of work relating cation fixation and release to the clay minerals and lattice expansion (Gruner, 1939; Page and Baver, 1940; Stanford, 1948; Barshad, 1948, 1950, 1954; Dyal and Hendricks, 1952; DeMumbrum and Hoover, 1958; Mortland, 1961). Neither would it explain why fixed K can be extracted with Ca or Na, but not with NH_4 (Hanway et al., 1957b). York (1949) found that fixation of K was apparently not microbial, as it was not affected by sterilization with chloropicrin.

DeMumbrum and Hoover (1958) studied changes in exchangeable K on drying of vermiculite, illite and mixtures of the two. They concluded that release of K on drying and reversion on re-wetting were due to the presence of illite, a release mineral; and vermiculite, a fixing mineral, within the same system. While this suggests the source of the K released on drying, it does not suggest the mechanism of release.

Scott et al. (1957) mention the possibility that K release on drying is due to exchange, but cite evidence from their own data both for and against such a mechanism. Further suggestions as to the mechanism of K release on drying have not been found in the literature.

MATERIALS AND METHODS

The soil material used for these studies, unless otherwise stated, was from the 36 to 48 inch depth of a Marshall profile. The site sampled was 400 ft. N., 165 ft. W. of the S.E. corner of N.W. 1/4 of N.E. 1/4 of Sect. 19, Clay Twp., Shelby County, Iowa. Two samples were obtained from this site, one in June and one in September, 1960. The moisture content of these samples was 22.5 and 24.3 percent, respectively. The exchangeable K content of the two samples was the same and they behaved alike in regard to K release and reversion. Thus, in reporting these studies, no distinction has been made between the two samples.

The soil was passed through a 1/8-inch sieve, mixed thoroughly and stored in plastic bags. No change in moisture content in storage was observed during the period of these studies. Throughout this manuscript only soils maintained at this moisture content will be termed "moist" or "undried". Samples that have been dried or dried and re-wetted will be designated as such. Soil moisture content was determined by drying 10 g. samples for 48 hours at 110° C. in a gravity-draft oven and was expressed as a percentage of the oven-dry weight of soil. All weights of Marshall subsoil mentioned in the manuscript are on an oven-dry basis.

Potassium was extracted with neutral 1N NH_4Ac which extracts both the exchangeable and water soluble K. The two

fractions have not been distinguished in these studies and for simplicity are termed exchangeable K.

To extract the exchangeable K, 25 ml. of NH_4Ac solution and 10 g. of soil, on an oven-dry basis, were placed in a flask and shaken for 30 minutes on a wrist-action shaker. The soil was then filtered and leached with further NH_4Ac to a final volume of 85 ml. Potassium was determined on a Perkin-Elmer Model 52C flame photometer using 500 ppm. of Li as an interval standard. Where oven-dry soils were extracted, they were cooled to room temperature over CaCl_2 before addition of the extractant. All data presented in the manuscript are averages of at least two determinations.

Ethanol used in these studies was of the "absolute" grade obtained in bulk. Other additions were of the "technical" or "analytical" grade with the exception of hexanol which was of "practical" grade. Water added to the soil was distilled and de-ionized in an exchange column with the exception of that in the NH_4Ac extractant.

PERTINENT CHARACTERISTICS OF THE MARSHALL SUBSOIL

The Marshall subsoil was chosen for these studies because of its considerable capacity to release K on drying (Hanway *et al.*, 1960) and because of the ease with which it can be sieved and mixed in the moist state.

The exchangeable bases extracted by NH_4Ac from the moist, air-dried and oven-dried Marshall subsoil are presented in Table 1. The exchangeable K was increased from 27 to 210 ppm.,

Table 1. Exchangeable bases in the Marshall subsoil at different moisture levels

Condition of soil	Moisture (%)	pH	Exchangeable bases (ppm.)			
			K	Na	Ca	Mg
moist	22.5	6.34	27	42	7120	644
air-dried	3.2	--	130	42	7200	578
oven-dried	0	6.15	210	48	7280	600

an increase of 680 percent, by oven drying. Exchangeable Na was also increased by drying, but only 14 percent. The changes in exchangeable Ca and Mg were small compared to the total amounts that were extracted from either the moist or dried soil. It is therefore difficult to obtain an accurate measure of the effect of drying on these cations. In this experiment, however, there appeared to be nearly as much Ca released by drying as there was K. The exchangeable Mg appeared

to decrease on drying, but the results were not consistent with degree of drying and the changes were small relative to the increases in exchangeable K and Ca. Thus, there was no evidence in this experiment that a simple exchange of cations between the exchangeable and fixed states was responsible for the release of K that occurred on drying.

Several treatments were applied to moist, air-dried and oven-dried Marshall subsoil and the resulting exchangeable K values compared with those for the untreated soils. In one treatment 7 ml. of water was added to each 10 g. sample of air- and oven-dried soil after which the samples were kept at approximately 25° C. for 48 hours followed by extraction with NH_4Ac . In another treatment 500 ppm. of K in 10 ml. of aqueous solution was added to moist and oven-dried samples, after which they were kept at approximately 25° C. for 48 hours followed by extraction. In a third treatment K was applied and the samples kept at approximately 25° C. for 48 hours. The samples were then placed in a gravity-draft oven and dried at 110° C. for 48 hours. Data from this experiment are presented in Table 2.

Addition of water to an oven-dried soil and storing for 48 hours has decreased the exchangeable K from 210 to 106 ppm. This amounts to a decrease in exchangeable K (reversion) of 104 ppm. Where water was added to air-dry soil the reversion was less, but resulted in lower exchangeable K, than was the

Table 2. Exchangeable K in the Marshall subsoil as affected by drying, re-wetting and K additions

Soil sample	Exchangeable K (ppm.)			
	No treatment	H ₂ O added undried	K added undried	K added oven-dried
undried	27	--	290	318
air-dried	130	87	--	--
oven-dried	210	106	350	343

case with addition of water to oven-dry soil. It is noted that when air- or oven-dried samples were re-wetted, the resulting exchangeable K was not as low as that of the original undried soil. This agrees with the findings of Hanway and Scott (1957a) and Hanway et al. (1960) from studies of a number of Iowa soils. Where K was added to moist or oven-dried soil, a considerable portion was fixed. Addition of 500 ppm. K to a moist soil containing 27 ppm. of exchangeable K resulted, after two days of storage, in 290 ppm. of exchangeable K. The amount of K fixed was therefore 237 ppm. ($500 + 27 - 290$). After addition of K to the moist soil, drying caused less fixation than moist storage. However, after addition of K and water to an oven-dry soil, re-drying resulted in more fixation than moist storage.

The data for the exchangeable K in oven-dry soil presented in Tables 1 and 2 were obtained by drying the soil for 48 hours. This drying period was selected because it was

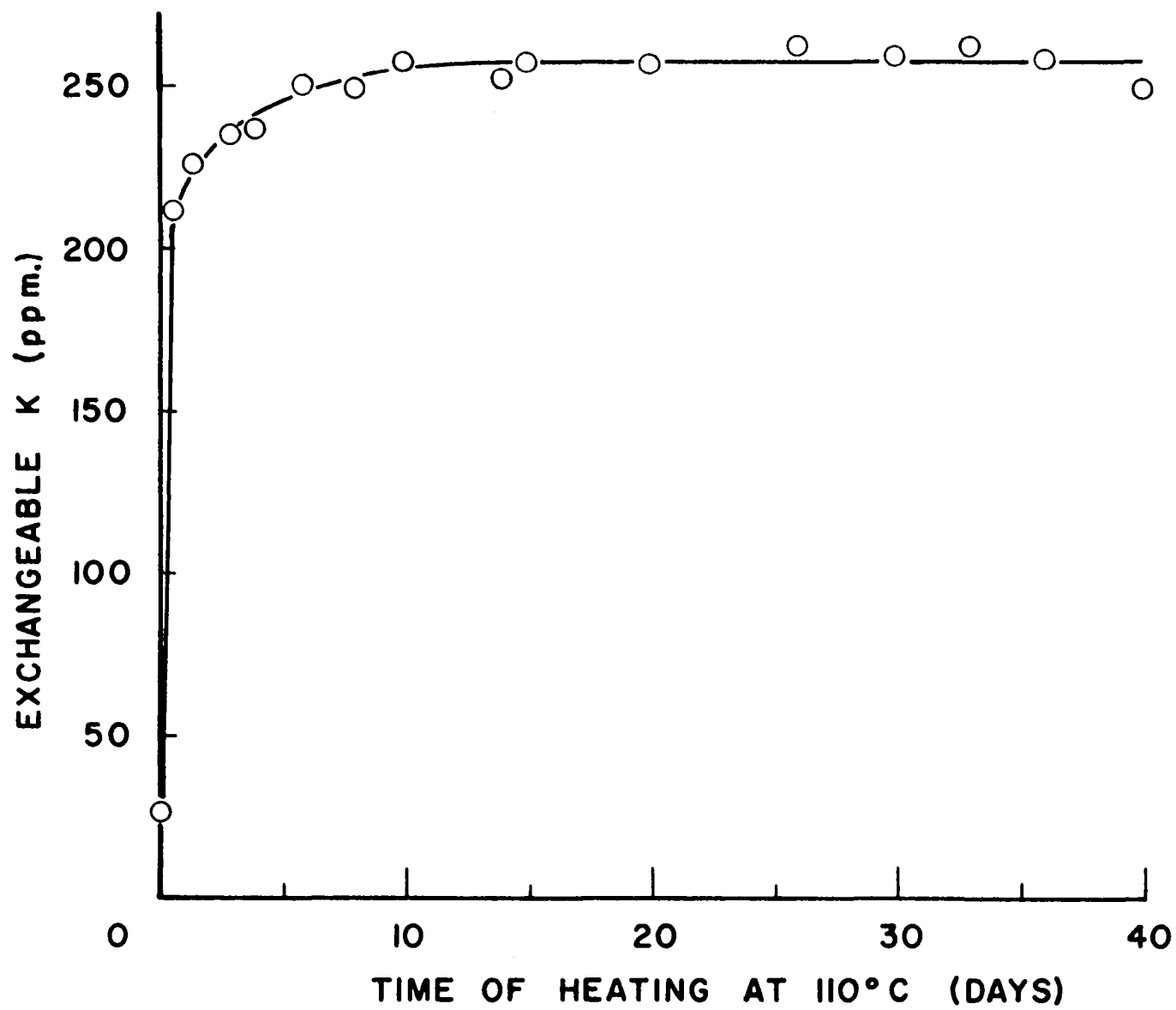
expected that the changes in exchangeable K with time would be relatively small thereafter. To verify this, and to obtain a better understanding of the changes in exchangeable K that occur with drying time, an experiment was conducted in which soil samples were dried at 110° C. for different periods of time.

A number of samples of the Marshall subsoil were placed in 50 ml. beakers and dried in a gravity-draft oven at 110° C. Samples were removed at selected time intervals and exchangeable K was extracted. This experiment was repeated three times. Average exchangeable K values are plotted against time of heating in Figure 1.

Large amounts of K were released in the first few hours of heating when water was being lost very rapidly. Thereafter the rate of release decreased until at the end of 15 days it appeared to be practically complete. This would indicate that with a single oven drying there is a limited amount of release which can occur. At the end of two days, the change in exchangeable K was less than 1 ppm. per hour. It was therefore concluded that 48 hours was a satisfactory heating period to be used for the rest of these studies.

In order to obtain a better understanding of the changes in exchangeable K with moisture loss, exchangeable K was determined in the Marshall subsoil at moisture levels ranging from field-moist to oven-dry (110° C.).

Figure 1. Exchangeable K in Marshall subsoil as affected by time of heating at 110° C. in a gravity-draft oven



To obtain moisture levels above three percent, the samples were left at room temperature but were partly covered to reduce the drying rate and thus produce more uniform drying within the sample. To obtain moisture levels of less than three percent, samples were heated slightly for a week or more by placing them near a steam hot-plate. The oven-dried (0 moisture) treatment received this same drying near the steam hot-plate followed by drying at 110° C. for 48 hours in a gravity-draft oven. Data from this experiment are presented in Figure 2.

It is apparent from Figure 2 that no K was released until the soil was dried considerably below the wilting point. This would suggest that, for the Marshall soil, the moisture content would not be reduced sufficiently by plant growth to release K by drying.

On drying, the exchangeable K started to increase at approximately eight percent moisture and continued to increase with moisture loss until the oven-dry state was reached. This pattern agrees with that presented by Scott et al. (1957) and with data of Reitemeier et al. (1948). It does not agree with findings of Lee (quoted by Scott et al., 1957) which showed no additional increase in exchangeable K on oven drying over that obtained by air-drying.

It is of interest to note that the exchangeable K values for the oven-dry samples of the same soil in Table 1 and

Figure 2. Exchangeable K in Marshall subsoil at different moisture levels

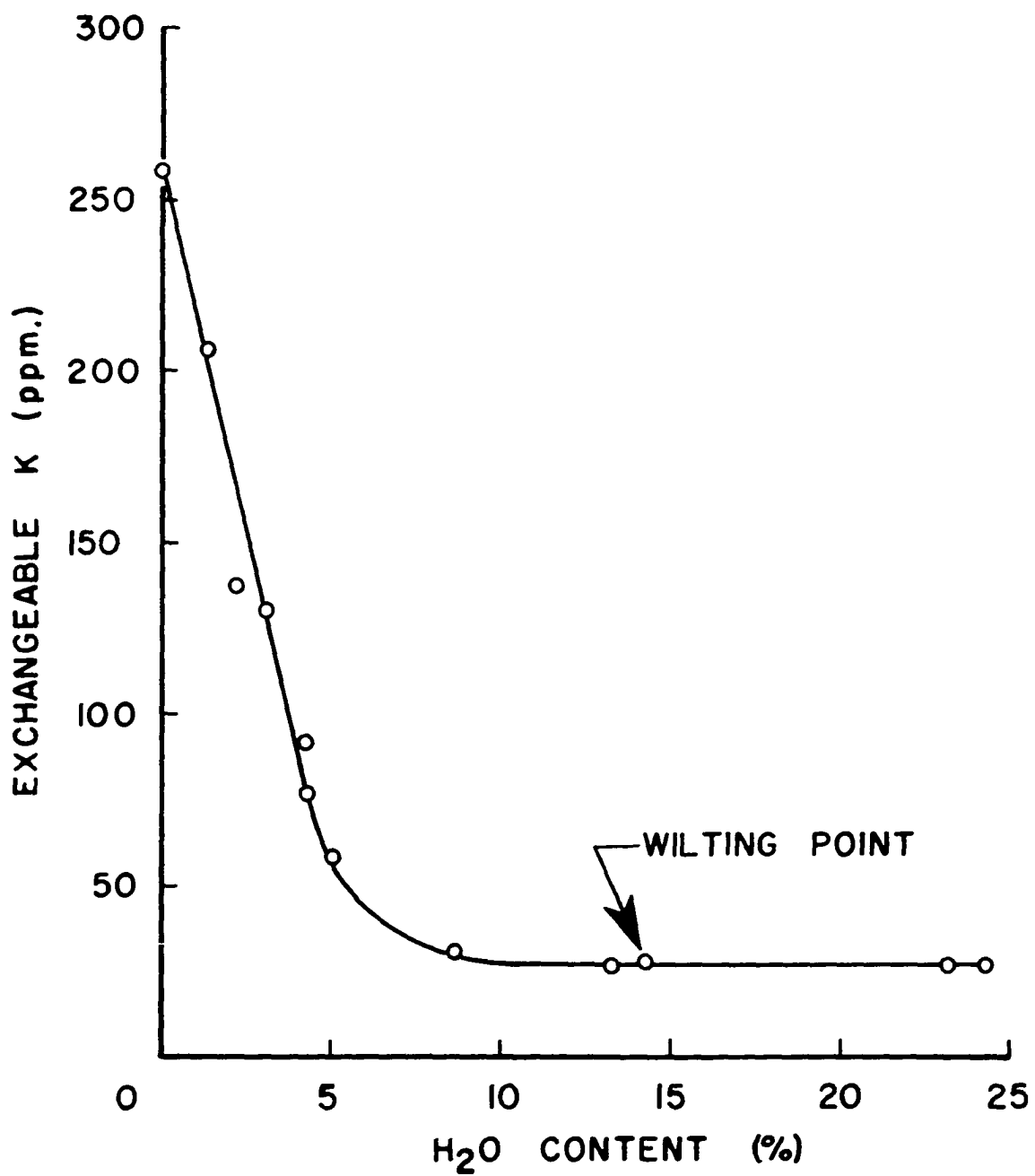


Figure 1 are different. The exchangeable K value presented in Table 1 was obtained by placing 10 g. samples of moist soil in 50 ml. beakers and heating them at 110° C. for 48 hours in a gravity-draft oven without previous drying. The value presented in Figure 1 was obtained by drying the soil near a steam hot-plate for more than a week followed by drying at 110° C. for 48 hours in a gravity-draft oven. Thus, the manner in which a soil is dried affects the amount of exchangeable K extracted after drying.

THE EFFECT OF MISCELLANEOUS SOIL TREATMENTS AND DRYING METHODS ON POTASSIUM RELEASE

In order to understand the mechanism of K release on drying, it appeared that more information was needed as to the effect of a wide range of soil factors and drying conditions on the quantity of K released. Information of this nature also appeared essential if means of controlling release on drying were to be found. A series of experiments of an exploratory nature was therefore conducted to study the effect of a number of treatments on K release.

Soil and Extractant Temperature

In preliminary experiments, differences were observed in the exchangeable K values determined for oven-dried soils at different times. It was considered possible that some samples had not been allowed to cool completely to room temperature before extraction and that this might be a cause of variation.

An experiment was conducted to study the effect of soil and extractant temperature on K extracted with NH_4Ac from oven-dry soil. All samples were dried in 125 ml. Erlenmeyer flasks at 110°C . for 48 hours in a gravity-draft oven. For one treatment 25 ml. of hot NH_4Ac (approximately 90°C .) was added to the sample directly on removal from the oven. The flask was then shaken for 30 minutes and leached with room temperature NH_4Ac to a final volume of 85 ml. For two other treat-

ments the flasks were cooled to room temperature and 2° C. followed by additions of 25 ml. of NH_4Ac at the respective temperatures. The flasks were then shaken and K extracted as described for the first treatment. Seven ml. of water at 90° C. was added to one treatment immediately on removal from the oven. Fifteen minutes later 25 ml. of room temperature NH_4Ac was added and the sample shaken and extracted as for the other treatments. Another treatment was cooled to room temperature, 7 ml. of room temperature water added, and 15 minutes later 25 ml. of NH_4Ac . The samples were then shaken and extracted as described for the other treatments. Room temperature was approximately 25° C. Data from this experiment are presented in Table 3.

Table 3. Exchangeable K extracted from oven-dried Marshall subsoil as affected by sample and solution temperature at the time of re-wetting

Soil Temp. (°C.)	H ₂ O Temp. (°C.)	NH ₄ Ac Temp. (°C.)	Exchangeable K (ppm.)
110°	--	90°	214
25°	--	25°	239
2°	--	2°	256
110°	90°	25°	114
25°	25°	25°	146

When the soil was extracted with room temperature NH_4Ac , the exchangeable K amounted to 239 ppm. Addition of water 15 minutes before the NH_4Ac extractant resulted in 146 ppm. of exchangeable K. Thus, 93 ppm. of K reverted to the non-exchangeable form in 15 minutes of moist storage. With soil and water temperatures at 110°C . and 90°C . respectively, reversion amounted to 125 ppm. leaving 114 ppm. of exchangeable K. Thus, in presence of water the exchangeable K was lower at higher temperatures due to increased reversion. Where only NH_4Ac extractant was added higher temperatures also resulted in lower exchangeable K values. It appears, therefore, that some reversion occurs in presence of NH_4Ac . These data showing lower amounts of K release at higher temperatures were in contrast to the data of Edwards (1960) which show increased release of NH_4 from bentonite as temperature is increased when NaCl or KCl extractants were used.

Since soil and extractant temperature affect the amount of K extracted, room temperature extractions were used in all other studies reported in this manuscript.

Drying Rate

In a previous section, a comparison of the data in Table 1 and Figure 1 showed that the exchangeable K content of the Marshall subsoil, after drying at 110°C . for 48 hours, varied with the method of drying.

To study these differences further, an experiment was conducted with treatments designed to give different rates of water loss at 110° C. To produce a very slow rate of water loss, 10 g. samples of Marshall subsoil were dried in 50 ml. beakers covered as tightly as possible with Al foil. Rapid drying was obtained by spreading the soil thinly on Al foil sheets and drying in a forced-draft oven. Three other treatments were applied to give intermediate rates of drying. The treatments are described in Table 4 along with the exchangeable K values for the dried soils.

The data show that less K was released as conditions for more rapid and more complete drying were introduced. It was shown in Figure 1 that more complete drying leads to greater release. Thus, the decrease in release shown in Table 4 must have been due to more rapid drying. This strongly suggests that release is not an instantaneous result of water loss, but takes some time to occur indicating that some sort of chemical reaction is probably involved.

The effect of drying rate on the amount of K released was overlooked for some time due to the results that were obtained with soils that were oven-dried after air drying. In several experiments treatments were included in which the soils had been air-dried to a constant moisture level before they were oven dried at 110° C. for 48 hours in a gravity-draft oven. These treatments were compared with others where

Table 4. Potassium released in the Marshall subsoil by drying at 110° C. for 48 hours as affected by drying conditions

Drying conditions	Exchangeable K in oven-dry soil (ppm.)	K released ^a (ppm.)
Gravity-draft oven, dried from 50 ml. beakers covered with Al foil	249	222
Gravity-draft oven, dried from 50 ml. beakers covered with Al foil with 1 pin hole in foil	242	215
Gravity-draft oven, dried from 50 ml. beakers covered with Al foil with a 1 cm. ² hole cut out	216	189
Gravity-draft oven, dried from open 50 ml. beakers	200	173
Forced-draft oven, dried from a thin layer of Al foil sheets	148	121

^aExchangeable K in the moist soil amounted to 27 ppm.

moist samples were oven-dried at 110° C. for 48 hours in a gravity-draft oven without previous air-drying. Average values from these experiments are summarized in Table 5.

The data in Table 5 show that air-drying of the soil before oven-drying did not increase the exchangeable K beyond that in the standard oven-dried treatment. It is, therefore, concluded that slower drying is effective in increasing K release, only at moisture levels below the air-dry state.

Table 5. Exchangeable K in the Marshall subsoil after oven-drying at 110° C. for 48 hours in a gravity-draft oven, as affected by previous air drying

Treatment before oven-drying	Exchangeable K (ppm.)
None	217
Air-dried	214

Since the drying method affects the exchangeable K values, it has been specified in the experiments presented in this manuscript. Exchangeable K data obtained from different methods of drying should not be compared directly.

Treatments that Tend to Disperse the Soil

It was observed by Scott et al. (1957) that addition of water to soil affected the release of exchangeable K on subsequent drying. Water added to soil causes some dispersion of the aggregates and it was considered possible that the two phenomena might be related.

An experiment was conducted to study the effect of water additions and stirring on exchangeable K content. Ten-gram samples of Marshall subsoil were placed in 125 ml. Erlenmeyer flasks. One treatment consisted of adding 7 ml. of water to each sample with as little disturbance as possible. In a second treatment 7 ml. of water was added, followed by

stirring and mixing with a rubber policeman. A third treatment received no water or mixing. Half of the samples treated in each of these two ways were then extracted with NH_4Ac while the other half were dried at 110°C . for 48 hours in a gravity draft oven followed by extraction. Data from this experiment are presented in Table 6.

Addition of water and stirring before extraction appeared to increase the exchangeable K slightly in the moist sample. Addition of water decreased release of K on drying and stirring produced an even greater decrease. While the reason for a decrease in release with stirring is not understood, it appears probable that addition of water has reduced release by this same stirring action, but to a lesser extent. It seems unlikely that the addition of 7 ml. of water has reduced K release by a reduction in the degree of drying. The time required for 7 ml. of H_2O to be lost at 110°C . is quite short and would be expected to have a negligible effect on the amount of K released.

Table 6. Exchangeable K in oven-dried Marshall subsoil as affected by addition of water and stirring before drying

Treatment	Exchangeable K (ppm.)		K released (ppm.)
	undried	oven-dried	
None	24	260	236
H_2O added	26	247	221
H_2O added, soil stirred	28	212	184

Several other treatments that disperse the soil to a greater or less extent were applied to the Marshall subsoil to study their effect on K release. These treatments will be discussed together.

The possibility exists that release of K on drying is due to a fracture of organic or oxide coatings on the clay minerals. If this were true, removal of organic matter and Fe and Al oxides might be expected to make more K available for extraction in the moist state. An exchange resin, "Dowex A-1 chelating resin", is reported by the manufacturers to be strongly selective for heavy and alkaline earth metals. Thus, it should be effective in removing Fe and Al coatings in the soil. This complexing resin has also been found by Bremner and Ho (1961) to lead to the removal of organic matter.

Fifty grams of moist Marshall subsoil was shaken for 30 minutes in water with 50 g. of Na saturated A-1 resin. The resin was greater than 80 mesh size and was readily separated from the soil by washing the latter through an 80 mesh sieve with water. The soil was then leached with water to remove soluble organic matter. No attempt was made to determine how completely the organic matter was removed. Two samples of the treated soil were extracted with NH_4Ac and two other samples were dried for 48 hours at 110°C . in a gravity-draft oven followed by extraction.

A second treatment consisted of removal of Fe_2O_3 by the

dithionite method of Jackson (1956). The method was modified in that a larger sample (60 g.) than that used by Jackson was treated and separations were carried out by filtering rather than centrifuging. Acetone treatment before the final separation, used by Jackson to flocculate the soil, was omitted. Two samples from this treatment were extracted with NH_4Ac without drying and two were oven-dried before extraction.

Soil samples were treated with high frequency sound to create a disruptive effect without the addition of chemical dispersing agents. By such treatment it has been found possible to reduce large mineral particles to colloidal dimensions (Eitel, p. 350, 1952). Ten-gram samples of soil were placed in the cup of a "Raytheon Magnetostriction Oscillator" Model S-102A. Twenty-five ml. of water was added and the machine operated for 0.5 hour at a plate voltage of 100 volts and maximum frequency for the machine. Two samples treated in this manner were extracted with NH_4Ac without drying and two were oven-dried before extraction.

Mixing the soil with water has been shown to reduce release of K (Table 6). The effect of mixing and dispersion and of adding water were tested further by adding 10 ml. of water to 10 g. samples of moist Marshall subsoil. Half of the samples were shaken for 12 hours on a wrist action shaker and the other half were left undisturbed for 12 hours. Both treatments were then oven-dried at 110°C . for 48 hours in a

gravity-draft oven. Another group of samples received these same treatments, except that the 10 ml. of water was replaced by 10 ml. of 2N NaCl.

The data from these treatments are presented in Table 7. Some of the oven-dried treatments were dried in 125 ml.

Table 7. The exchangeable K in undried and oven-dried Marshall subsoil as affected by treatments applied to the undried soil

Treatment	Exchangeable K (ppm.)		K released (ppm.)
	Moist	Oven-dried	
Erlenmeyer flasks			
Untreated soil	27	243	216
Treated with high frequency sound	62	206	144
H ₂ O added	--	229	--
H ₂ O added, shaken	--	195	--
NaCl added	--	136	--
NaCl added, shaken	--	129	--
Beakers			
Untreated soil	27	210	183
Dowex A-1 resin treated ^a	52	157	105
Dithionite treated	54	154	100

^a Dowex A-1 chelating resin supplied by courtesy of the Dow Chemical Company, Midland, Michigan.

Erlenmeyer flasks and some in 50 ml. beakers. The effect of drying is different in the two containers due to differences in drying rate (Table 4). The treatments dried by the two methods have therefore been separated in Table 7 and the data obtained from standard, or check, treatments are presented for each drying method.

From the data presented in Table 7, it is apparent that addition of water before drying caused a reduction in the exchangeable K in the dried soil and shaking with water, a further reduction. This confirms the findings reported in Table 6. It is concluded that dispersion or disturbance of the soil causes a reduction in K release and that the reduction in K release resulting from addition of water is probably due to dispersion.

The sound treatment increased the exchangeable K in the moist soil quite markedly, but decreased the amount of K released. The increase in moist exchangeable K would suggest that sound treatment has caused some disruption of the clay mineral lattice. The reduction in K release due to sound treatment is believed to be due to disturbance of the soil.

Addition of NaCl before drying decreased the exchangeable K in the oven-dried soil by nearly 50 percent. This agrees with the findings of Scott et al. (1957) in studies with Harpster and Fayette soils. In the presence of NaCl, shaking produced a smaller reduction in the exchangeable K of

the oven-dried soil than in the presence of water. This would suggest that dispersion was not a big factor causing reduction in K release on drying with NaCl. With the rates of NaCl used, the soils would be quite saline and would not be expected to disperse readily.

The Dowex A-1 resin and dithionite treatments produced almost identical effects; both markedly increased the exchangeable K in the moist soil and reduced the release of K. Both these treatments result in partially Na saturated soil and it is likely that the reduction in K release was largely due to the presence of Na. It is probable that dispersion, caused by the shaking, required in both treatments, also caused some reduction in release.

Treatment with H₂O₂ before Drying

Most surface soils do not release as much K on drying as do subsoils (Hanway and Scott, 1957a; Hanway et al., 1960) and this is true for the Marshall soil. Scott and Hanway (1960) found that glycerol added to the soil blocked release of K on drying and it will be shown that certain other organic compounds have the same effect. Since the surface soil does not release as much K on drying as the subsoil, and is much higher in organic matter, it was believed possible that organic compounds in the surface soil might be blocking release. Marshall surface soil was therefore treated with H₂O₂ to

destroy as much of the organic matter as possible and the effects of this treatment on K release on drying were studied.

Ten-gram samples of moist surface soil were placed in 50 ml. beakers and 5 ml. of H_2O added with 3 ml. of 30% H_2O_2 . After the most vigorous reaction had subsided, the samples were heated on a steam hot plate. Three ml. additions of H_2O_2 were made, followed by heating, until the color of the soil had changed quite markedly. Two more additions were made after the color change appeared to be complete. Most of the free liquid was then evaporated off on the steam plate. One group of samples was leached with 30 ml. of H_2O after which half were extracted with NH_4Ac and the remaining half were dried at $110^\circ C.$ for 48 hours in a gravity-draft oven followed by extraction. A second group of samples was not leached with water and was divided into two treatments, one of which was extracted with NH_4Ac and the other was oven-dried followed by extraction. Data from this experiment are presented in Table 8.

It is apparent that the H_2O_2 treatment has increased the exchangeable K in the moist soil and decreased the exchangeable K in the oven-dry soil, resulting in a very small release of K on drying. This agrees with the findings of Merwin and Peech (1951) and would suggest that if organic compounds were blocking release in the surface soil, they were not removed by H_2O_2 treatment. Dispersion of the Marshall subsoil was

Table 8. Potassium released by the Marshall surface soil as affected by H_2O_2 treatment of the undried soil

Treatment	Exchangeable K (ppm.)		K release (ppm.)
	undried	oven-dried	
Untreated soil	172	264	92
Soil treated with H_2O_2	224	248	24
Soil treated with H_2O_2 then leached with H_2O	170	197	27
H_2O leachate from above treatment	60		

shown to produce similar effects as those shown here with the surface soil. It is possible that the effect of H_2O_2 is due to dispersion of the soil.

Surface soils are usually considerably higher in exchangeable K than subsoils. This would appear to be a logical reason for the smaller amount of release on drying with surface soils since it has been shown that where high rates of K are added, K is actually fixed on drying (Scott *et al.*, 1957). It is interesting to note, however, that when the exchangeable K of the moist H_2O_2 treated sample was reduced by leaching, there was little or no effect on the amount of K released by drying.

Drying in Different Gaseous Atmospheres

It was considered possible that release of K on drying might be associated with oxidation of various materials in the soil. If this were so, changes in the supply of oxygen during drying would affect the amount of K released. To test this possibility, samples of the Marshall subsoil were dried in atmospheres of different gases.

Duplicate samples of moist soil were placed in small metal tins which were then placed in large pyrex test tubes maintained in a horizontal position. Gas was passed through drying tubes then through the test tubes containing the soil samples and finally bubbled into a container of water. The rate of flow was controlled to give the same rate of bubbling for each of the four gases used. The soil samples were placed in the test tubes and gas passed through for 15 minutes at 25° C. The test tubes containing the samples were then placed in a gravity-draft oven and heated at 110° C. for 48 hours. Gases were passed through the test tubes at a slow rate throughout the heating period. Air, helium, oxygen and carbon dioxide were the gases used. Data from this experiment are presented in Table 9.

It is apparent that changing the atmosphere in which the soil was dried did not affect the amount of K released.

Table 9. The effect of different atmospheres during oven-drying on exchangeable K content of oven-dried Marshall subsoil

Atmosphere during drying	Exchangeable K (ppm.)
Air	213
Helium	216
Oxygen	212
Carbon Dioxide	219

Successive Dryings and Extractions

When the Marshall subsoil is oven-dried, the exchangeable K increases from 27 to 210 ppm., an eight-fold increase. This is only a small part of the total K in the soil. It was of interest, therefore, to determine how much K would be released if after drying the K were removed and the soil dried again and if this sequence of drying and extraction were repeated a number of times.

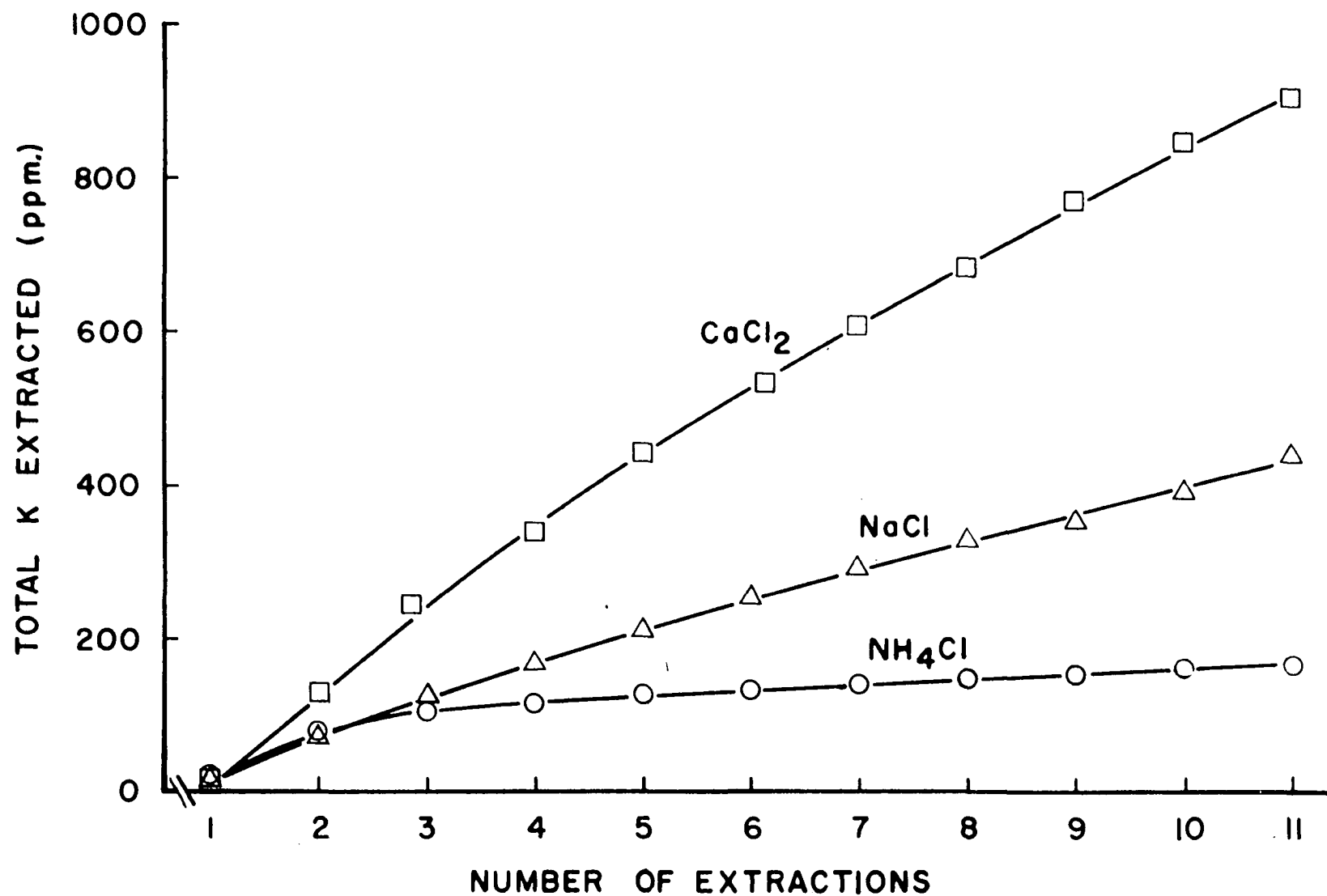
Evans and Simon (1950) in a similar study with Miami, Spencer and Carrington soils found more K released if the soil was H saturated than if it was NH_4 saturated before drying. It was shown by Scott et al. (1957), however, that the release of K was largely blocked by the presence of added NH_4 . Sodium chloride and HCl additions reduced the amount of K that was released, but to a lesser extent. Calcium, Mg and La

salt additions on the other hand had no effect (Scott and Hanway, 1961). Therefore an experiment was conducted in which K release was measured following successive dryings and extractions. The K released was extracted with NH_4 , Na and Ca to vary the blocking effect of the cations on the exchange complex.

Ten-gram samples of moist Marshall subsoil were extracted with 0.1 N solutions of CaCl_2 , NaCl and NH_4Cl . CaCl_2 and NaCl solutions were prepared from salts containing less than 0.01 percent and less than 0.00 percent K, respectively. Drying and extraction treatments were repeated alternately until eleven extractions and ten dryings had been completed. To extract the exchangeable K, a small volume of extractant was added to the dry soil and shaken by hand for not more than two minutes. This limited time of shaking, compared to 30 minutes in other experiments, was used to minimize the reversion of K expected where Ca and Na extractants were used. As soon as the soil was completely broken up by shaking, it was poured on a filter in a Buchner funnel and leached to a final volume of 85 ml. Potassium was determined in each extract and the cumulative curves for K removed by successive dryings and extractions are presented in Figure 3.

The NH_4Cl solution removed more K from the undried soil than NaCl or CaCl_2 (21, 6 and 7 ppm., respectively). When the soil was saturated with these cations and oven-dried, however, Ca removed the most K and NH_4 the least. The order $\text{Ca} > \text{Na} >$

Figure 3. Total K extracted from the Marshall subsoil by successive extractions and dryings. Samples were alternately extracted with 0.1 N salts and dried for 48 hours at 110° C. in a gravity-draft oven



NH_4 for the amount of K removed by each drying and extraction sequence persisted throughout the experiment resulting in quite marked differences in the total amounts of K removed (910, 421 and 165 ppm. K by Ca, Na and NH_4 , respectively). These results are consistent with observations of Scott et al. (1957) and Scott and Hanway (1961) that the blocking effect of these cations on K release by drying is in the order $\text{NH}_4 > \text{Na} > \text{Ca}$.

The amount of K removed per extraction with CaCl_2 decreased only slightly with successive dryings and extractions. Thus it appeared that the soil would continue to release K if the same procedure were continued for many more dryings and extractions. A similar pattern was noted for Na. With NH_4 the amount of release per extraction decreased more rapidly as extractions and dryings were repeated and appeared to be constant after the fourth drying at approximately 6 ppm. of K per extraction.

The NH_4 ion was most effective in extracting K from the moist soil and least effective in extracting K after drying. It appears, therefore, that the differences in amount of K extracted by the different cations after drying are due to the presence of the cations during drying rather than to differences in their ability to extract K. It was shown that K continued to be extracted on successive dryings and extractions and that different cations extracted different amounts

of K. It appears that no particular limited amount of K within the soil is susceptible to release, but that the amount of release is affected by the cations on the soil.

THE EFFECT OF ORGANIC ADDITIVES ON POTASSIUM RELEASE

It has been reported by Scott and Hanway (1960) that additions of various solvents may affect the amount of K released on drying and that glycerol may inhibit release completely. These results suggest that organic additives may be useful in controlling release on drying and as a tool with which more may be learned about the release process. Further investigations on the effects of these and other additives were therefore undertaken.

Dielectric Constant

According to Coulomb's law $F = \frac{e_1 e_2}{Dr^2}$ where e_1 and e_2 are two electrical charges at a distance r apart. The force, F , acting between the charges is thus inversely proportional to the dielectric constant of the medium, D . Therefore, if e_1 is the charge on a K ion and e_2 is the charge on the clay lattice, the attraction between them will be inversely proportional to the dielectric constant of the liquid medium, usually water. If K release on drying is an exchange reaction, it would appear that changing the medium, and hence the dielectric constant, might change the amount of K released.

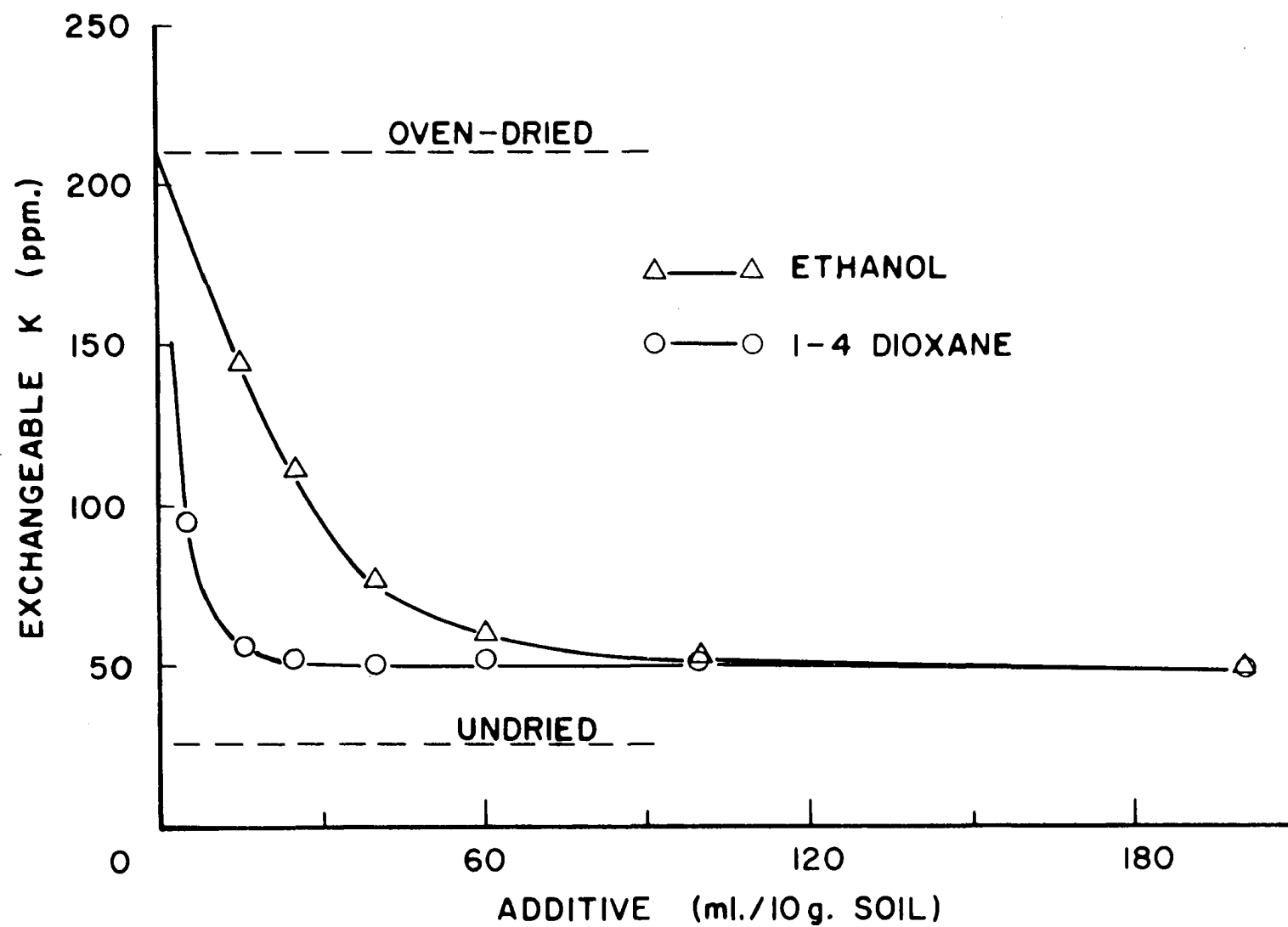
Water, which has a high dielectric constant (78.5), has been shown to permit considerable release of K from the Marshall subsoil on drying. Most organic compounds have much

lower dielectric constants than water. Therefore, if dielectric constant is important as a factor in the reduction of K release by organic compounds, dioxane with a low dielectric constant (2.2) should be quite effective. Ethanol with a dielectric constant intermediate between those of dioxane and water (24.3) should be considerably less effective than dioxane in reducing K release.

To compare the effects of 1-4 dioxane and ethanol on K release, these compounds were added at varied rates to 10 g. samples of moist Marshall subsoil. Samples and additive were dried in 50 ml. beakers when the rate of addition was less than 40 ml. For higher rates of addition the smallest beaker that would hold the additive and soil was used. All samples were heated on a steam hot-plate until most of the free liquid had evaporated. They were then transferred to a gravity-draft oven and dried at 110° C. for 48 hours. Data from this experiment are presented in Figure 4.

At lower rates of addition it is apparent that dioxane was slightly more effective than ethanol but as the rate of addition was increased, the two became equally effective. Both compounds markedly decreased the amount of K release with increasing rate of addition at lower rates, but as the amount added is increased over 100 ml. of ethanol, or 25 ml. of dioxane, little further change is observed. If dielectric constant were an important factor affecting the amount of K

Figure 4. Exchangeable K in Marshall subsoil dried at 110° C. for 48 hours in a gravity-draft oven after additions of ethanol and dioxane



release, the two compounds should have produced quite different effects at higher rates of addition where the ratio of water to additive would be small. It appears that under the conditions studied, dielectric constant is not an important factor affecting release of K in presence of organic compounds.

Preliminary Studies with a Range of Compounds

In order to determine what types of compounds are effective in preventing K release, a wide range of compounds were added to the moist Marshall subsoil followed by drying at 110° C. for 48 hours in a gravity-draft oven. Where rates of addition were high, 25 ml. or more, the samples were heated on a steam hot-plate until most of the free liquid had evaporated before placing them in an oven at 110° C. Mannitol and inositol were added to the soil in 14 and 28 ml. of water, respectively. Other compounds which are not liquid at room temperature were added in 7 ml. of water. Data from this experiment are presented in Table 10.

All of the compounds listed in Table 10, except acetone, reduced the amount of K released in the Marshall subsoil. The size of the reduction in exchangeable K varied considerably from one compound to another. Ammonium acetate did not block K release completely and, at the rates used, appeared to be approximately equal to the amino acids in effectiveness. The lower molecular weight normal alcohols were not very

Table 10. Exchangeable K in Marshall subsoil as affected by addition of various compounds prior to drying at 110° C. for 48 hours in a gravity-draft oven

Chemical compound	Amount added/10 g. soil		Exchangeable K (ppm.) ^a
	(ml.)	(moles)	
none			210
methanol	200		130
ethanol	200		49
n-propanol	60		34
n-hexanol	7		27
n-octanol	7		17
cyclohexanol	7		27
3-methyl cyclohexanol	7		25
3-methyl-1-hexanol	7		26
ethylene glycol	7		34
glycerol	7		28
sucrose		0.007	27
mannitol		0.007	88
phenol	7		38
inositol		0.007	93
acetone	25		212
cyclohexanone	7		29
cyclopentanone	7		34
propionaldehyde	20		189
1-4 dioxane	200		48
gelatin	0.14 g.		157
glycine		0.007	64
l-proline		0.007	66
B-alanine		0.007	72
pyridine	7		55
triethanolamine	7		37
NH ₄ Ac		0.01	69

^aUndried soil contained 27 ppm. of exchangeable K.

effective in blocking K release, but those of higher molecular weight were quite effective. Cyclohexanol and related compounds as well as glycerol and sucrose were also quite effective. The higher molecular weight alcohols, glycerol, sucrose and similar compounds would appear to merit further study.

The Marshall subsoil was leached with a group of liquid compounds in an effort to determine their effect on K release. Some of these compounds, such as ether and benzene, are not very soluble in water. The soil was therefore leached with acetone and then with the less soluble compound. This was done in the belief that acetone would remove soil water and that the less water soluble compound, ether or benzene, would remove the acetone. By this treatment it was considered possible that the soil would be left with only the last solvent present at the time of drying. Reagent grade absolute alcohol was used in all except one of the experiments reported in this manuscript. In this one experiment the absolute ethanol used had been dehydrated by refluxing with CaO and CaCl_2 for 12 hours in an N_2 atmosphere. The alcohol was then distilled directly onto samples of Marshall soil and allowed to leach through them after which the samples were dried at 110°C . This treatment was applied to determine if water might be present in the absolute ethanol causing a reduction in its effectiveness in preventing release of K.

In treatments where solvents were added to the soil samples, and not removed by leaching, most of the excess free liquid was evaporated by heating on a steam hot-plate. All samples were then placed in a gravity-draft oven and heated at 110° C. for 48 hours. Data from these treatments are presented in Table 11.

Table 11. Exchangeable K in Marshall subsoil as affected by leaching with various solvents followed by drying at 110° C. for 48 hours in a gravity-draft oven

Compound added	Amount and method of addition	Exchange- able K ^a (ppm.)
None	--	210
ethanol	200 ml. added	49
ethanol	leached with 100 ml., added 100 ml.	50
ethanol	leached with 500 ml., then with 500 ml. dehydrated	48
1-4 dioxane	200 ml. added	48
1-4 dioxane	leached with 100 ml., added 100 ml.	42
acetone	25 ml. added	212
acetone	leached with 85 ml.	69
acetone-ether	leached with 85 ml. acetone then 85 ml. ether	69
acetone-benzene	leached with 85 ml. acetone then with 85 ml. benzene	68
ether	leached with 85 ml.	218
benzene	leached with 85 ml.	228
CCl ₄	leached with 85 ml.	224
n-hexane	leached with 85 ml.	228

^aUndried soil contained 27 ppm. of exchangeable K.

Data for large additions of ethanol and dioxane are also presented in Table 11 to provide a comparison of K release where these compounds were applied to the soil or leached through it. Addition of 200 ml. of ethanol appeared to be as effective in preventing K release as leaching with 100 ml. followed by addition of 100 ml. Dehydrated ethanol was no more effective in reducing K release than smaller amounts of untreated ethanol. Leaching and addition of dioxane was slightly more effective than addition alone. Leaching with acetone was much more effective than addition, but the rate used was much higher. Ether, CCl_4 and hexane had little or no effect on K release.

It has been shown in Tables 10 and 11 that a wide variety of compounds affect K release on drying, but to varying degrees. In order to determine why some compounds are more effective than others, their physical constants were examined. The molecular weight, boiling point, dielectric constant and dipole moment of some of these compounds are presented in Table 12.

By comparing the amount of K released from the soil in presence of dioxane and ethanol (Figure 4) it was shown that dielectric constant, under the conditions studied, was not closely related to the effect of organic compounds on K release. From Tables 10 and 12, it can be seen that several compounds, for example glycerol and n-hexanol, have dielectric

Table 12. Physical constants of certain organic compounds

Compound	Molecular weight	Boiling point at 1 atm. °C.	Liquid ^a dipole moment (Debye units)	Liquid ^b dielectric constant	Solubility ^c in H ₂ O g./100 ml.
Water	18	100	3.1	78.5	∞
methanol	32	65	3.0	32.6	∞
ethanol	46	78	2.9	24.3	∞
propanol	60	97	3.1	20.1	∞
n-butanol	74	118	2.9	17.1	7.9
primary isobutanol	74	108	2.9	17.7	10 ^{15°}
secondary butanol	74	100		15.8	12.5
tertiary butanol	74	83	1.7	10.9 ^{30°}	∞
n-hexanol	116	157		13.3	0.59
n-octanol	130	195	3.0	10.3 ^{20°}	0.054
cyclohexanol	100	162	2.8	15.0	5.67 ^{15°}
glycerol	92	290	0.3	42.5	∞
ethylene glycol	62	197	3.5	37.0	∞

^aObtained from Wesson, L. G. 1948. Values at 18-45° C.

^bObtained from Maryott, A. A. and Smith, E. R. 1951. Values at 25° C. unless stated.

^cObtained from Chemical Rubber Publishing Co. 1957-1958. Values at 25° C. unless stated.

Table 12. (Continued)

Compound	Molecular weight	Boiling point at 1 atm. °C.	Liquid ^a dipole moment (Debye units)	Liquid ^b dielectric constant	Solubility ^c in H ₂ O g./100 ml.
acetone	58	56	2.9	20.7	∞
1-4 dioxane	88	102	0.0	2.2	∞
ethyl ether	74	35	1.3	4.3 ^{20°}	7.5
benzene	78	80	0.0	2.3	0.082 ^{22°}
carbon tetrachloride	154	77	0.0	2.2	0.08

constants intermediate between dioxane and water, but even at low rates of application they resulted in considerably lower exchangeable K values after drying than dioxane. This provides further evidence that the dielectric constant was not closely related to the effect of organic compounds on K release.

The other constants listed in Table 12 may be worth examining. In each case this should be done in relation to water since their effect on K release is determined by comparison with drying of soils containing only water. Dipole moments of glycerol and dioxane are both low, but the former is quite effective in preventing K release and the latter only moderately so. Octanol and methanol both have dipole moments almost as high as water, but one is quite effective and the other rather ineffective in preventing release. Within the range studied the dipole moment of a compound does not appear to be closely related to its ability to affect release of K.

Examination of the solubility data shows that glycerol and ethanol are both very soluble in water, but differed markedly in their effect on K release. Benzene and octanol are both rather insoluble, but the one did not affect release at all and the other prevented release completely under the conditions studied. Solubility in water, therefore, does not appear to be related to the effect of organic compounds on release of K.

In general the release of K appears to decrease with increasing molecular weight of the additive over the range presented. Carbon tetrachloride was an exception as it has a high molecular weight but did not affect release of K. Dioxane, ethyl ether, and benzene also appeared to be somewhat less effective than they should be on the basis of molecular weight alone. It is interesting to note that these compounds which were exceptions all have boiling points lower than water.

A general study of the boiling points indicates that they increase with the ability to prevent K release. Ethylene glycol is an exception as its ability to prevent K release was slightly less than hexanol or octanol which have lower boiling points. However, the molecular weight of ethylene glycol is much lower than those of hexanol or octanol. Of the constants listed, boiling point and molecular weight are correlated with the ability of additives to block release of K on drying. Boiling point appears to be the major factor in this group.

Alcohol and Sugar Additions

Evidence presented in the preceding section showed that alcohols and sugars were effective in blocking release of K in soils on drying. Studies were therefore undertaken to learn more about these compounds and how they should be used to block release of K. Different rates of addition were com-

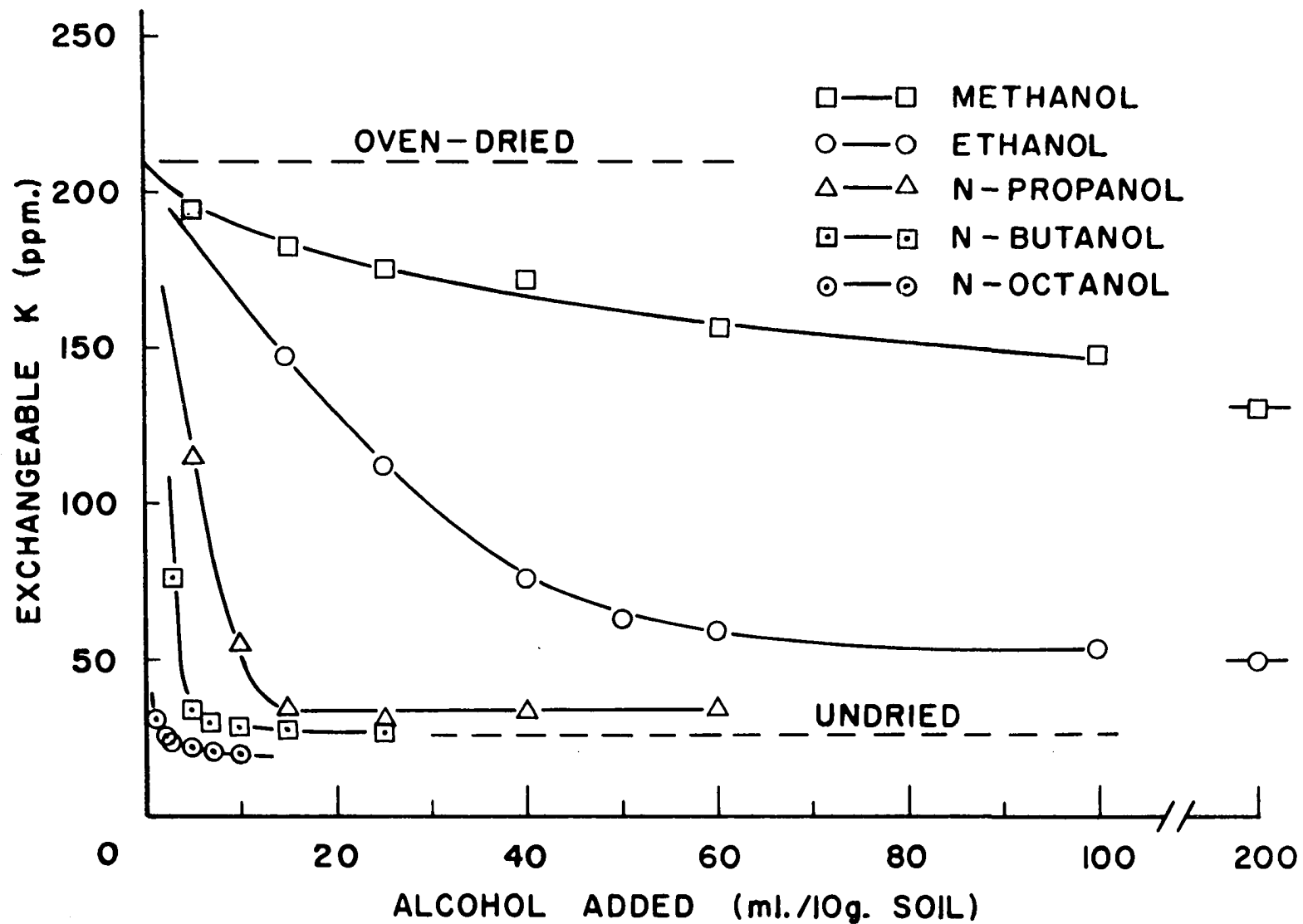
pared with a number of compounds to determine the optimum rate of addition and to provide comparisons between the different compounds at various rates. Compounds with ranges of molecular weight and boiling point were studied as well as compounds with the same molecular weight, but different molecular configuration.

The normal alcohols provided a range in ability to block release of K and a range in molecular weight without the confounding effect of differences in molecular configuration or number of hydroxyl groups. Experiments were therefore conducted to study their effect, at varied rates of addition, on K release on drying.

Methyl, ethyl, n-propyl, n-butyl and n-octyl alcohols were added to the Marshall subsoil at varied rates before drying at 110° C. for 48 hours in a gravity-draft oven. Samples with alcohol additions of 40 ml. or less were dried in 50 ml. beakers. For higher rates of addition the smallest beaker that would hold the sample and solvent was used. To reduce the fire hazard, butanol and alcohols with lower molecular weight were heated on a steam hot-plate to evaporate most of the excess free liquid before placing in the oven at 110° C. Data from this experiment are presented in Figure 5.

The longer chain alcohols were more effective in blocking K release than those with shorter chains applied at the same rates. For example, at the 25 ml. rate, butanol completely

Figure 5. Exchangeable K in Marshall subsoil dried at 110° C. for 48 hours in a gravity-draft oven after additions of normal alcohols

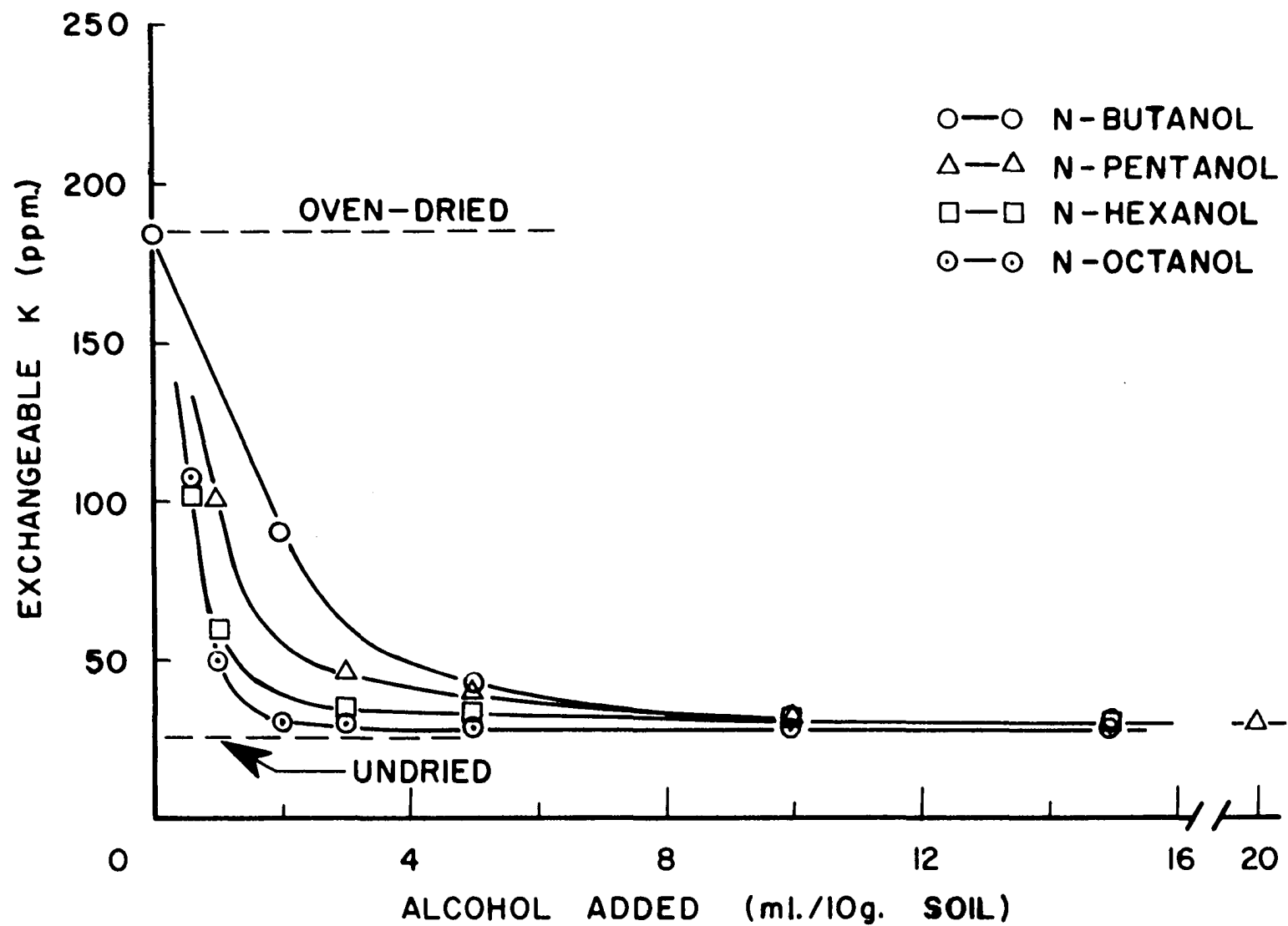


blocked release of K, but methanol produced only a small reduction in release. Not only did the longer chain alcohols permit less release than those with shorter chain length at low rates of addition, but the maximum effect of the longer chain alcohols in preventing release was greater than those with shorter chain length. Soil treated with propanol reached a minimum exchangeable K value after drying of 34 ppm. When octanol was added, the minimum level was 20 ppm. of exchangeable K, less than in the undried sample (27 ppm.). As both molecular weight and boiling point increase with chain length, it is not possible to determine from this experiment which was more important in determining the effectiveness of alcohols in preventing release. It is apparent, however, that under the conditions studied, longer chain alcohols are more effective in preventing K release.

Alcohols with higher boiling points, such as octanol (B.P. 195° C.), dried slowly in the gravity-draft oven, particularly at high rates of addition. Therefore a series of normal alcohols with higher boiling points were added to the Marshall subsoil at varied rates and dried at 110° C. for 48 hours in a forced-draft oven. Data from this experiment are presented in Figure 6.

The curves showing exchangeable K plotted against additions of normal alcohols for drying in the forced-draft oven (Figure 6) are similar, in general shape, to those for the

Figure 6. Exchangeable K in Marshall subsoil dried at 110° C. for 48 hours in a forced-draft oven after additions of normal alcohols



gravity-draft oven (Figure 5). However, they have been displaced to the right and slightly upward. This indicates that when soils were dried in a forced-draft oven more alcohol was required to prevent the exchangeable K from exceeding a given level and the minimum exchangeable K with any one alcohol was reduced. Butanol, for example, did not completely prevent release of K in the forced-draft oven, even at the highest rates of addition, but in the gravity-draft oven it did. Octanol caused fixation of K on drying in the gravity-draft oven, but did not in the forced-draft. Without addition of any additive it was shown (Table 4) that the faster drying occurring in the forced-draft oven, compared with the gravity-draft oven, resulted in less K being released. With the addition of additives which reduced the amount of K released, the reverse was apparently true. In the presence of alcohols more K was released when the soil was dried rapidly in the forced-draft oven than when it was dried more slowly in the gravity-draft oven.

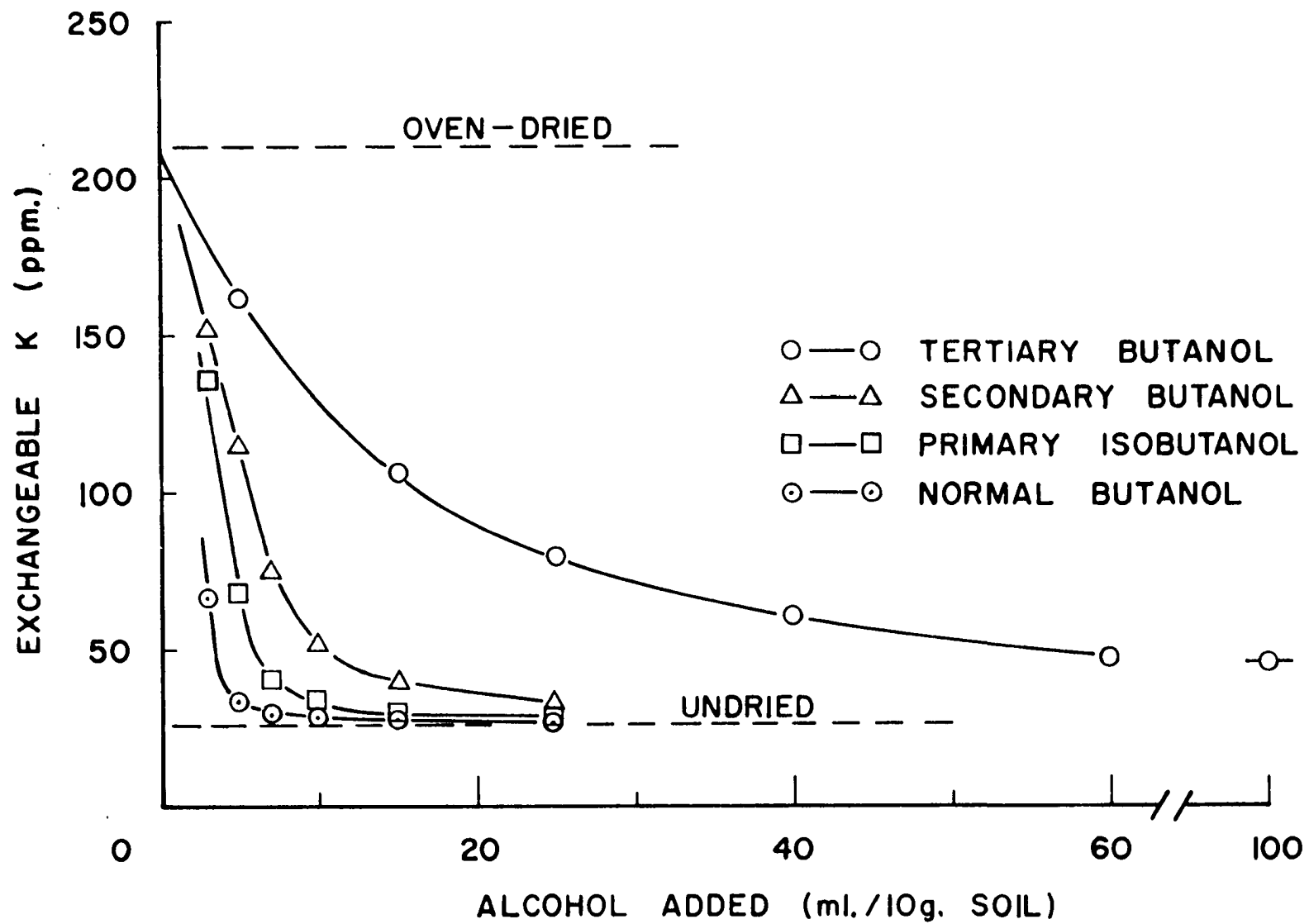
When it was found that the effect of alcohol additions on K release by drying increased with the length of the straight carbon chains, a study was initiated to determine if branching of the carbon chain also had an effect. The butyl alcohols were used in this study as they provide different molecular configurations with the same molecular weight and number of hydroxyl groups.

Different rates of the four butanols were added to the Marshall subsoil before drying at 110° C. for 48 hours in a gravity-draft oven. Samples were heated on a steam hot-plate until most of the excess free liquid was evaporated off, before being placed in the oven at 110° C. Curves showing the changes in exchangeable K with rates of butanol are presented in Figure 7.

From these curves it is apparent that for alcohols with more branching of the carbon chain larger additions were required to prevent release beyond a given level and the minimum exchangeable K obtainable after drying decreased. Normal butanol at the rate of 25 ml. per 10 g. of soil prevented release of K completely whereas 100 ml. of tertiary butanol per 10 g. of soil did not. The boiling points of the butanols vary with the amount and position of the branching, the less branched butanols having higher boiling points. It is therefore difficult to determine whether degree of branching or boiling point is more important in preventing release. From these data it would appear that the molecular weight of the alcohol is not a major factor determining its effect on K release. Also it is evident that, under the conditions studied, straight-chain alcohols are more effective in preventing K release on drying than the branched chains alcohols.

It was shown (Table 10) that sucrose and glycerol were

Figure 7. Exchangeable K in Marshall subsoil dried at 110° C. for 48 hours in a gravity-draft oven after additions of butanols



among the more effective compounds tested for preventing K release on drying. The effect of these compounds at different rates was therefore determined.

Ethylene glycol, glycerol, dextrose and sucrose at different rates were added to sufficient water to provide 14 ml. of solution, and placed in 50 ml. beakers. Ten grams of Marshall subsoil was then added to each beaker and the samples dried at 110° C. for 48 hours in a gravity-draft oven. Sucrose and dextrose treatments were taken to dryness on a steam hot-plate before placing in the oven at 110° C. This largely overcame the tendency for larger sugar additions to caramelize. Data from this experiment are presented in Figures 8 and 9.

In Figure 8 the amount of material added is expressed in moles. Sucrose, dextrose and glycerol resulted in practically complete blocking of release when added in sufficient quantity. Ethylene glycol was not capable of blocking release completely even at the highest rate tested. Ethylene glycol is more volatile than glycerol, while sugars are not volatile. Thus, the boiling point of ethylene glycol would suggest that it should be less effective. The molecular weight is also quite low. The amount of glycerol required to produce the maximum effect in blocking release was greater than for dextrose which was greater than for sucrose. Thus, on a molar basis, sucrose was more efficient in blocking K release on drying than any of the other compounds tested.

Figure 8. Exchangeable K in Marshall subsoil dried at 110° C. for 48 hours in a gravity-draft oven after additions of ethylene glycol, glycerol and sucrose

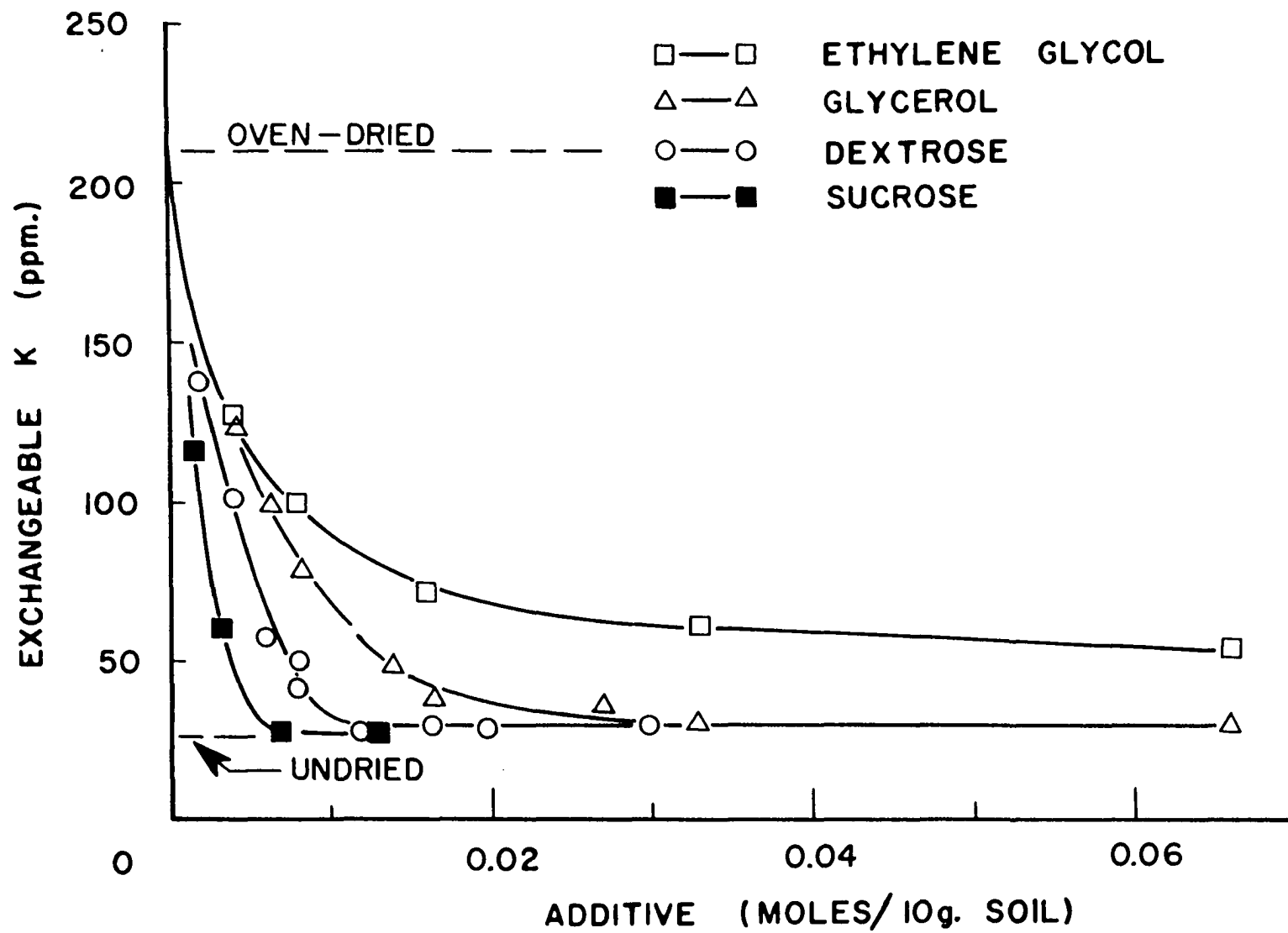
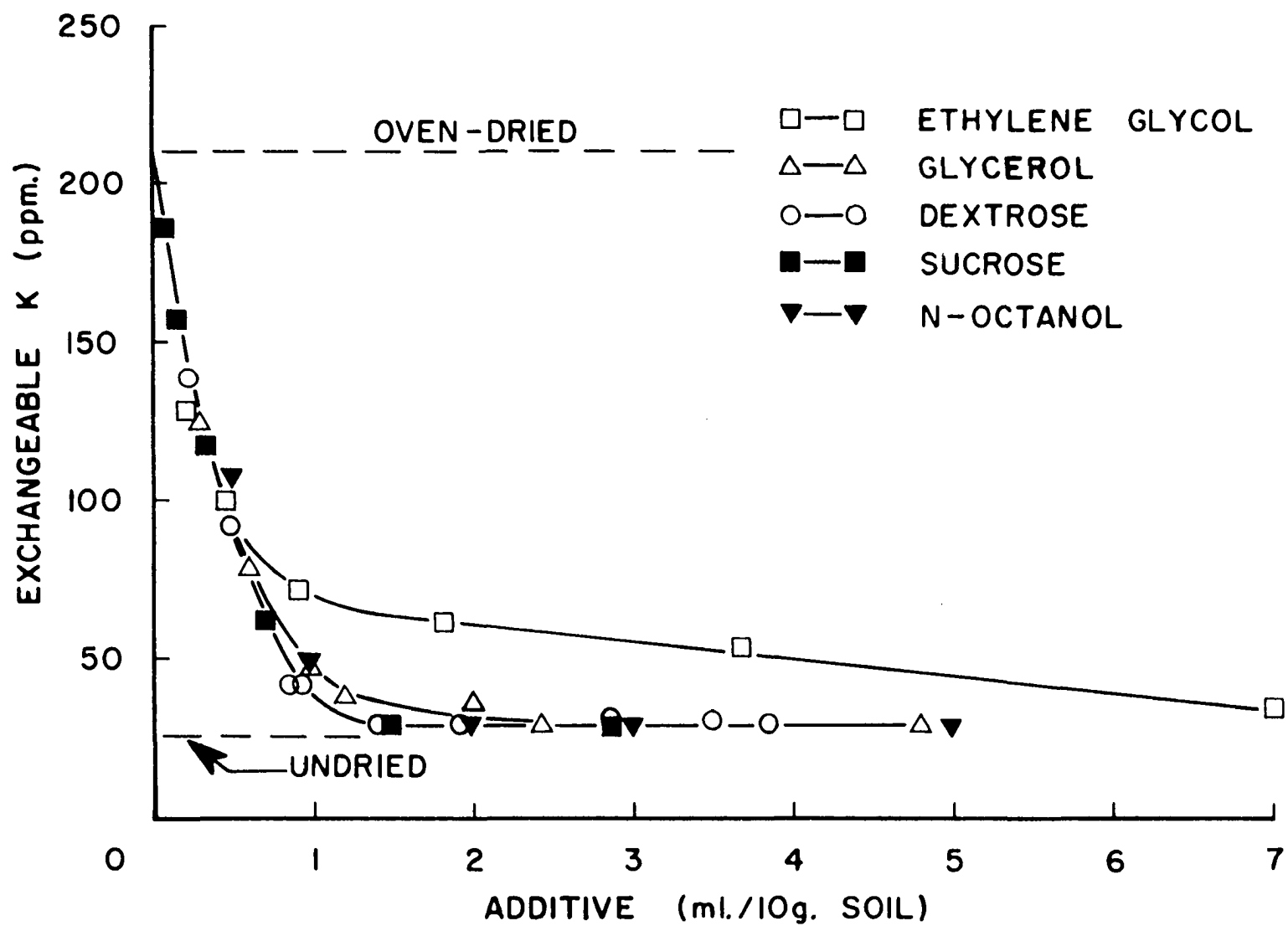


Figure 9. Exchangeable K in Marshall subsoil dried at 110° C. for 48 hours in a gravity-draft oven after additions of ethylene glycol, glycerol, n-octanol and sugars



In Figure 9 the amount of material added is expressed in milliliters. Since glycerol and glycol are liquids, their rate of application was measured by volume. The rates of sugars were measured by weight and the volumes were computed by dividing the weight added in g. by the density in g. per c.c. Density values of 1.544 and 1.588 g. per c.c. for dextrose and sucrose were obtained from the Chemical Rubber Publishing Co. (1957-1958). Exchangeable K data obtained on addition of octanol and drying in a forced-draft oven (from Figure 6) are also included in Figure 9.

It is apparent that on a volume basis, sucrose and dextrose were equally effective in preventing release. Glycerol and octanol were slightly less effective than the sugars at lower rates of addition. Both glycerol and octanol are volatile to some extent and it seems probable that the lower effectiveness of these compounds was simply due to smaller amounts being present than were added due to losses by vaporization during drying. It would appear that the manner in which these compounds affect release is more physical than chemical. If it were a chemical reaction, it would be expected that the effectiveness of different compounds would be more similar when amounts were plotted on a molar basis. The fact that octanol with only one hydroxyl group is as effective as glycerol with three would suggest that their effectiveness is not related to chemical reactions with the hydroxyl group.

The amount of glycerol required to form a monolayer in the soil was determined by the method of Diamond and Kinter as described and modified by Mehra and Jackson (1959). It was found that 0.35 ml. of glycerol was required to form a monolayer compared with approximately 2 ml. of glycerol or 1.5 ml. of sucrose required to prevent release. It appears that considerably more than a monolayer of organic compound is required to block release.

The Role of Water in the Effectiveness of Organic Additives

The boiling point of alcohols has been shown to be rather closely related to their ability to reduce release of K. The more effective compounds for reducing K release are those with boiling points considerably above that of water. Even with some of these compounds, it has been shown (Figures 5 and 6) that they are less effective in blocking release if drying occurs in a forced-draft oven. Since release of K appears to be related to water loss, organic compounds probably prevent release only if they are present on the soil while water is being lost. Compounds with higher boiling points would be expected to evaporate more slowly than water and thus be present on the soil until after the water is lost. This would explain why compounds with higher boiling points are more effective in preventing K release. It might also explain why most com-

pounds are less effective in preventing release when dried in a forced-draft oven than when dried in a gravity-draft oven. In the forced-draft oven evaporation is more rapid and much of the organic compound probably is lost before all the water is gone.

An experiment was conducted with some of the lower boiling point compounds to study effects of water additions on release in presence of organic additives. One series of treatments consisted of leaching Marshall subsoil with 100 ml. of various compounds followed by addition of a further 100 ml. of these same compounds and drying at 110° C. for 48 hours in a gravity-draft oven. In a second series of treatments the soils were leached with 100 ml. of the same compounds followed by addition of 90 ml. of the compounds and 10 ml. H₂O. Before drying in the oven all samples were heated on a steam hot-plate until most of the excess free liquid had evaporated. Data from this experiment are presented in Table 13.

It is apparent that the effectiveness of the compounds with lower boiling points, such as methanol, ethanol and acetone, has been reduced markedly by addition of water. As the boiling point of the additive increased, water no longer reduced its effectiveness in blocking K release. Where 10 ml. of water was added the time required for all of the water to evaporate would be greater. Thus, more of the organic additive would evaporate before the water was all gone. Additives

Table 13. Exchangeable K in the Marshall subsoil after drying at 110° C. for 48 hours, as affected by leaching and addition of organic liquids, alone or with water, before drying

Organic liquid	Exchangeable K (ppm.)	
	dried from 100 ml. organic liquid	dried from organic liquid + H ₂ O
methanol	64	189
ethanol	50	113
acetone	56	153
1-4 dioxane	42	52
n-propanol	42	37
n-butanol	38	33

with lower boiling points, such as methanol, were probably largely lost before the water had all evaporated. The fact that water additions did reduce the effectiveness of additives in preventing K release, and that this effect was more pronounced with the lower boiling point additives, would suggest that the additives must be present until the water is gone to be effective.

Another experiment was conducted to determine the effect of methanol, ethanol and dioxane on K release on drying when added with different amounts of water. Ten-gram samples of the Marshall subsoil were added to 100 ml. aliquots of organic compounds with varied rates of water. The samples were heated

on a steam hot-plate until most of the excess free liquid was driven off and were then dried at 110° C. for 48 hours in a gravity-draft oven. Data from this experiment are shown in Table 14.

Table 14. Exchangeable K in Marshall subsoil after drying at 110° C. for 48 hours in a gravity-draft oven, as affected by the amount of water added with organic compounds before drying

Organic compound	H ₂ O added (ml.)	Exchangeable K (ppm.)
methanol	0	150
"	1	161
"	5	177
"	20	184
ethanol	0	52
"	1	51
"	5	64
"	20	181
1-4 dioxane	0	50
"	1	50
"	5	53
"	20	54

It is apparent that the effectiveness of these additives in preventing K release was reduced by the presence of water and that this effect was proportional to the amount of water added.

An experiment was conducted to determine the effect of adding water with compounds having high boiling points. Samples of Marshall subsoil were leached with 50 ml. of six different solvents. Ten ml. of water was then added to half

of the samples and all treatments were dried at 110° C. for 48 hours in a forced-draft oven. Data from this experiment are presented in Table 15.

Table 15. Exchangeable K in the Marshall subsoil after drying at 110° C. for 48 hours in a forced-draft oven, as affected by leaching with organic compounds and addition of water before drying

Organic compound	Boiling point (°C.)	H ₂ O added (ml.)	Exchangeable K, (ppm.)
glycerol	290	0	42
"		10	43
ethylene glycol	197	0	66
"		10	88
octanol	195	0	30
"		10	31
cyclohexanol	162	0	37
"		10	48
hexanol	157	0	30
"		10	62
cyclohexanone	156	0	34
"		10	102

Glycerol and octanol were as effective in blocking K release with water added as without. From the data in Table 15 it is apparent that the lower the boiling point of an additive the more addition of water reduces its ability to block release of K on drying. This effect is more consistent for the additives studied than is the relationship between boiling point and the ability of the additive to block release.

The ability of ethylene glycol to prevent K release was more affected by addition of water than would be predicted from the boiling point. Without water, however, it is also less effective in preventing K release than its boiling point would suggest it should be, in relation to other compounds. Data presented in Table 15 were obtained by drying in a forced-draft oven. They therefore showed the compounds tested to be less effective in preventing K release than they were shown to be in data obtained by drying in a gravity-draft oven. Drying in the forced-draft oven may also have accentuated differences due to addition of water.

Since some of the higher boiling point compounds were as effective when water was added as when it was not, it appeared that they might give the same results in a gravity-draft as in a forced-draft oven. Treatments dried in gravity-draft and forced-draft ovens were therefore compared. Samples were placed in 50 ml. beakers and after addition of the organic compounds they were dried at 110° C. for 48 hours. Data are presented in Table 16.

The data on dextrose are particularly interesting. At the rates tested the effectiveness of dextrose in blocking K release was not affected by the amount of water added or the method of drying. Since dextrose is not volatile at the temperatures used, it would be present until all the water was driven off regardless of method of drying or amount of water.

Table 16. Exchangeable K in the Marshall subsoil after drying at 110° C. for 48 hours in forced-draft and gravity-draft ovens, as affected by the addition of various compounds before drying

Addition before drying	Amount of aqueous solution (ml.)	Exchangeable K (ppm.)	
		gravity-draft oven	forced-draft oven
dextrose 0.02 moles	10	30	29
" "	50	30	30
dextrose 0.03 moles	10	30	32
" "	50	30	31
n-octanol - 1 ml.	none	31	50
" - 5 ml.	"	22	28
cyclohexanol - 1 ml.	"	44	55
" -10 ml.	"	29	37
n-butanol - 5 ml.	"	34	43
" -15 ml.	"	28	30

These characteristics would appear to make dextrose an ideal compound to use for preventing K release.

The other compounds tested were less effective in preventing K release when dried in a forced-draft oven than when dried in a gravity-draft oven. The higher the rate of addition the smaller was the difference in exchangeable K between drying methods. This would be expected if the water must be lost before the additive is lost to block release, and if the forced-draft oven tends to mask the differences in rate of evaporation between the organic additive and water, as was suggested earlier.

Data have been presented which suggest that the boiling

point of organic compounds is closely related to their ability to prevent release of K. It appears probable that this relation exists because the additive must remain on the soil while water is being lost in order to prevent release. Compounds with boiling points much higher than water may be expected to remain on the soil longer, and thus less K is released. If the effectiveness of the additive is controlled chiefly by its ability to remain on the soil, however, boiling point is probably not the only factor which would cause differences in the ability to prevent release.

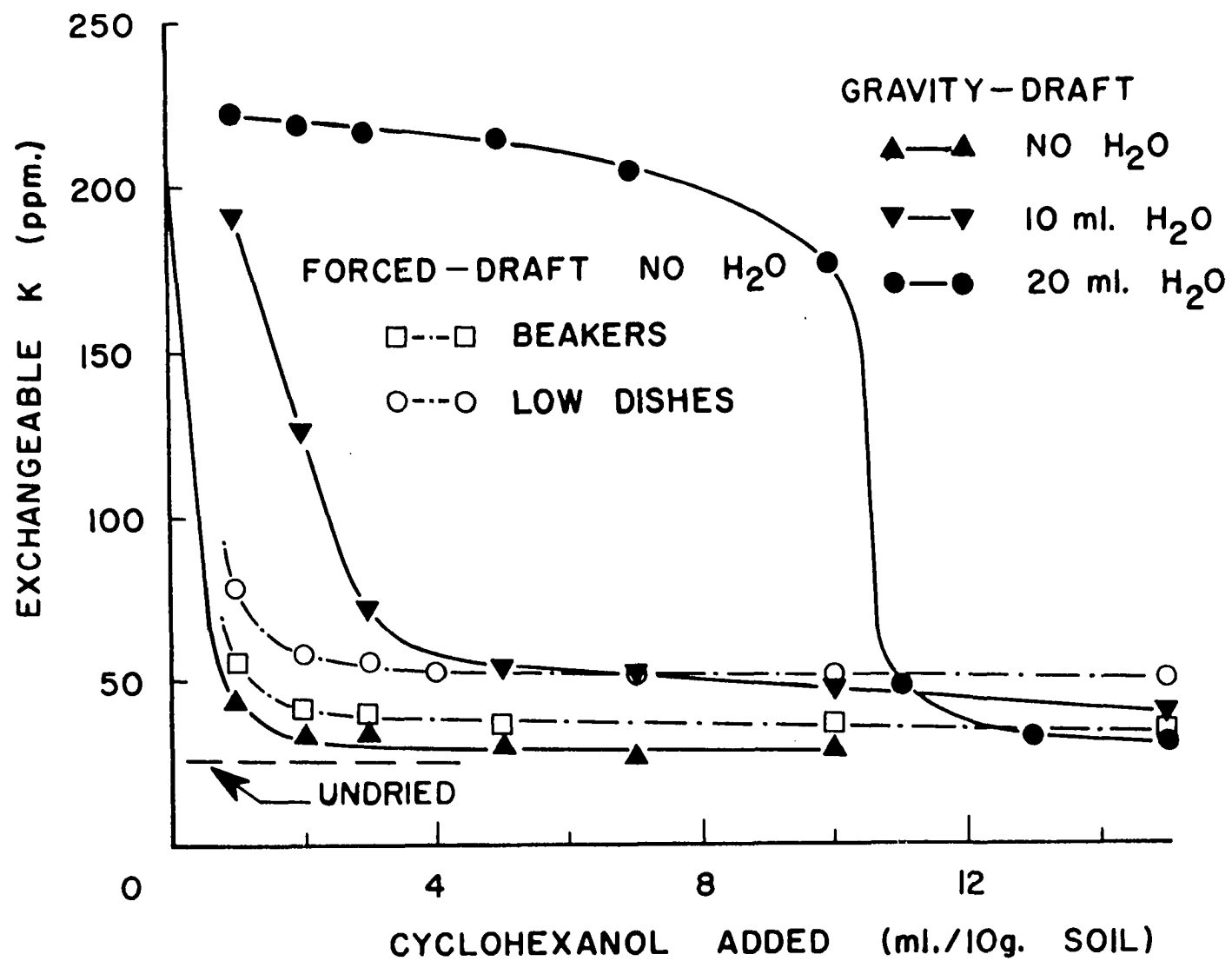
Hofman and Brindley (1960), among others, have described clay-alcohol complexes. The strength of the complex is affected by molecular shape. Thus, the shape should affect the rate at which any complexed alcohol is lost on heating and whether it is lost faster than water. Hofman and Brindley conclude from their work that adsorption increases with chain length up to 10 carbon atoms. This could explain why the straight chain alcohols hexanol and octanol (Table 15) were more effective in blocking release of K on drying in the forced-draft oven than their boiling points would suggest they should be, in relation to other additives.

It has been suggested that the amount of K release depends on whether the water or organic additive is lost from the soil first. An investigation where both the rate of organic additive and the rate of water addition are varied

over a considerable range should provide a better picture of these relations. An experiment was carried out in which different rates of cyclohexanol along with 0, 10 and 20 ml. of water were added to samples of Marshall subsoil in 50 ml. beakers. The samples were then dried at 110° C. for 48 hours in a gravity-draft oven. To provide faster drying rates for comparison, cyclohexanol was added to samples of the Marshall subsoil in 50 ml. beakers and in low dishes, 6.6 cm. in diameter and 8 mm. high. These samples were then dried at 110° C. for 48 hours in a forced-draft oven. Data from these treatments are presented in Figure 10.

When no cyclohexanol was applied the exchangeable K amounted to 210 ppm. in the gravity-draft oven and 185 ppm. in the forced-draft oven. From the curves presented it is apparent that when no water was added, cyclohexanol was more effective in blocking K release in the gravity-draft oven than in the forced-draft oven. At the 5 ml. rate, cyclohexanol was almost completely effective in blocking K release in the gravity-draft oven resulting in 30 ppm. of exchangeable K. At the same rate of addition in the forced-draft oven exchangeable K was approximately 37 ppm. Where the drying was from low dishes in the forced-draft oven, cyclohexanol was even less effective in blocking K release, resulting at the 5 ml. rate, in approximately 53 ppm. of exchangeable K. It appears that the faster the sample was dried the less effec-

Figure 10. Exchangeable K in the Marshall subsoil after drying at 110° C. for 48 hours in forced and gravity-draft ovens as affected by different rates of water and cyclohexanol added prior to drying



tive cyclohexanol became, in preventing K release.

It has been shown (Table 16) that the effect of drying rate was greater with more volatile compounds. This effect is believed to be related to water. Where the drying rate is slow the less volatile component, cyclohexanol in this experiment, will evaporate more slowly than the water and is believed to remain on the soil until more of the water is lost. It is suggested that where the rate of evaporation is greater, as in the forced-draft oven, the difference in volatility is minimized so that some water is still on the soil when most of the additive is gone. Potassium is then believed to be released when this water is lost without the presence of additive.

Where water was added with the cyclohexanol, the amount of the latter required to limit the exchangeable K to a certain level was greater than where no water was added. This agrees with the findings presented in Tables 14 and 15 for cyclohexanol and more volatile compounds. When the amount of water added was increased from 10 ml. to 20 ml. the effect of cyclohexanol on K release followed a rather unusual pattern. With 20 ml. of water added, cyclohexanol at low rates of addition had very little effect on K release, but when the rate of addition approached 10 ml. per 10 g. of soil, the cyclohexanol rather suddenly became quite effective in reducing K release. Cyclohexanol and water form a low boiling

point azeotrope. Therefore, if the mixture of cyclohexanol and water on the soil contains a higher proportion of water than the azeotropic mixture, the latter should be lost on heating and the remaining mixture would become higher in water content. In this case virtually no blocking of K release would be expected. On the other hand when the amount of cyclohexanol is increased sufficiently, the mixture will be lower in water and higher in cyclohexanol than the azeotrope. Heating should again cause the azeotropic mixture to be lost, but in this case the remaining mixture would become more concentrated in cyclohexanol. Thus, cyclohexanol would probably remain until after the water had been driven off. It is believed that this may be the cause of the sudden break observed in the curve formed by plotting exchangeable K against cyclohexanol with 20 ml. of water added. The minimum boiling point azeotrope, however, forms at 80 percent water or a water cyclohexanol ratio of 4:1, whereas the rates of water to cyclohexanol at the point where exchangeable K began to decrease rapidly was approximately 2:1. The reason for this difference is not understood.

The minimum exchangeable K obtainable by addition of cyclohexanol appeared to be the same whether water was added or not. This would be expected if the cyclohexanol only needs to be present until after the water has been lost to prevent release.

It was shown that the effectiveness of alcohols in preventing K release was moderated by rate of drying and the amount of water added, or originally present in the soil. Even differences in the number of samples dried in a particular oven, especially with large additions of water, have been found to affect the rate of drying and consequently the exchangeable K values obtained. These difficulties can be overcome by using non-volatile additives such as dextrose as was seen from the data in Table 6.

From the data which have been presented, it appears that the most important factor in preventing release of K on drying is to have an organic compound present while water is being driven off. If this is so, even the less effective compounds tested should be capable of preventing release of K completely if they can be maintained on the sample until the water is driven off. High rates of addition or leaching with ethanol or dioxane did not block release completely (Table 11). It is possible, however, that these compounds did not replace the adsorbed water, under these conditions, leaving some water to be lost after the alcohol had evaporated.

An experiment was carried out with ethanol to determine whether release might be blocked even with this compound if it could be maintained on the sample while water was lost. Ten-gram samples of Marshall subsoil were placed in 50 ml. beakers and dried at 75° C. for 48 hours in a gravity-draft

oven as a check treatment. A second treatment consisted of adding 25 ml. of ethanol to the soil followed by drying at 75° C. In the third treatment samples were kept covered with ethanol for 24 hours at 75° C. and then allowed to dry for 24 hours at 75° C. The samples were kept covered by adding ethanol each time the level of liquid on the samples became low. A fourth treatment was kept covered with ethanol and heated at 75° C. for 48 hours. Soil samples for the fifth treatment were placed in 50 ml. beakers and 25 ml. of ethanol added. The beakers were then kept in an atmosphere nearly saturated with ethanol. This was accomplished by placing the sample container on a stand in a 600 ml. beaker which was covered with a watch glass held approximately 1/8 inch above the rim of the beaker. Ethanol was placed in the bottom of the large beaker and replenished when required. These samples were heated, along with the others, for 48 hours at 75° C. This temperature was chosen because ethanol could not be maintained on the sample at a temperature above its boiling point (78° C.) at 1 atmosphere pressure. Data from this experiment are presented in Table 17.

It is noted that drying at 75° C. increased the exchangeable K from 27 to 159 ppm. After addition of 25 ml. of ethanol followed by heating the exchangeable K amounted to 45 ppm. However, when the soil was kept covered with ethanol for 24 hours while it was heated to remove water, the

Table 17. Exchangeable K in Marshall subsoil after heating with ethanol at 75° C.

Treatment	Exchangeable K (ppm.)
None	27
Moist soil, dried 48 hours	159
Moist soil + 25 ml. ethanol, dried 48 hours	45
Moist soil kept covered with ethanol for 24 hours at 75° C. then allowed to dry 24 hours	29
Moist soil, kept covered with ethanol for 48 hours	20
Moist soil + 25 ml. ethanol, heated in an atmosphere nearly saturated with ethanol for 48 hours	16

resulting exchangeable K was approximately the same as for the undried soil. Thus, when ethanol was kept on the soil for 24 hours, it completely blocked release of K.

Ethanol maintained on the soil for 48 hours either as free liquid, or as nearly saturated vapour, at 75° C. caused the exchangeable K to drop below that of the original moist soil. Thus, in ethanol at 75° C. some of the exchangeable K was fixed. This suggests the possibility that both fixation and release of K can occur on drying (H₂O removal) in the same soil at one time. It appears that fixation may be observed if release is prevented by the presence of alcohol.

Alcohols have been found to differ markedly in their

ability to reduce K release when applied to the soil and allowed to evaporate during drying. It is suggested that these differences are largely dependent on whether these alcohols are lost from the soil before or after water in the drying process. The data presented in Table 17 provide strong support for this concept. It seems probable that the factors most important in determining whether they are lost before or after water on heating at 110° C. are the boiling point, or volatility, of the additive and its affinity for the clay mineral. If the additive is maintained on the soil, it appears that even compounds with low boiling points will completely prevent release. Under such conditions boiling point is probably of no significance in relation to K release.

Effect of Organic Additions on K Extraction

A number of the experiments which have been presented show that lower exchangeable K values are obtained with oven-dry Marshall subsoil if various organic materials are added before the samples are dried. These results have been interpreted as showing that additives reduce the release of K which otherwise would occur on drying. It is possible, however, that K release did take place in presence of these compounds, but that the added material simply interfered with extraction of the K. To do this the additive would have to be present on the soil after a period of 48 hours in an oven

at 110° C. An experiment was therefore conducted to determine if the additive, or a residual effect from it, still remained on the soil after oven-drying.

Ten-gram samples of the Marshall subsoil were treated with various organic compounds and oven-dried. In the case of the more volatile alcohols, methyl and ethyl, the soil was leached with 100 ml. followed by addition of 100 ml. Other materials were added without leaching. Half of the samples were extracted after 48 hours of drying at 110° C. The remainder were re-wet with 7 ml. of water, re-dried at 110° C. for 48 hours in a gravity-draft oven and then extracted. Data from this experiment are presented in Table 18.

When no organic material was added, there was slightly less exchangeable K in the sample that was oven-dried, re-wet and oven-dried again than in the sample that was only oven-dried once. The lower exchangeable K observed with the re-dried sample is believed to be due to the water that was added. It has been shown (Table 6) that addition of water reduces release of K. It was presumed that the samples treated with organic compounds and dried would also release K if they were re-wet with water and re-dried provided there was no additive, or residual effects of the additive, remaining on the sample at the time of re-drying. The data in Table 18 show, however, that the amounts of exchangeable K extracted did vary with the additive. The more volatile alcohols had only a small effect

Table 18. Effect of organic additives applied to Marshall subsoil before drying, on the exchangeable K after drying at 110° C. for 48 hours, and after addition of water and re-drying

Additive	Amount applied (ml.)	Exchangeable K (ppm.)	
		Additive applied dried	Additive applied, dried
			H ₂ O added re-dried
gravity-draft			
none		210	202
methanol	200	64	186
ethanol	200	50	181
n-octanol	7	17	43
sucrose	0.007 moles	27	34
n-hexanol	1	54	207
	3	26	167
	5	24	159
	7	24	160
	10	22	157
cyclohexanol	3	36	172
	10	30	177
forced-draft			
none			188
cyclohexanol	3	42	163
	10	38	163
n-pentanol	1	100	182
	3	40	168
	5	32	164
	7	30	162
	10	30	162

on the exchangeable K extracted from the re-dried samples. Most of these alcohols would probably evaporate during the first drying. Those materials that were more effective in blocking K release during the first drying, however, also showed considerable effect in the second drying. More of these materials persisted through the first drying, as might be expected since they were more effective in blocking release.

From this experiment it can be concluded that some of the compounds do persist in the soil throughout the 48 hour drying period and might, therefore, interfere with extraction of K released during drying.

Since some of the organic additives do persist in the soil, their effect on K extraction was studied further by adding them to moist and oven-dried soils. Several of the less volatile additives were added to moist Marshall subsoil. Half of the samples were then extracted with NH_4Ac and half were dried at 110°C . followed by extraction. The same additives were applied to oven-dry samples of the Marshall subsoil followed by 7 ml. of water. These samples were stored at room temperature for 8 hours before extraction. Glycerol and cyclohexanol were added to oven-dry samples followed one hour later by extraction. Data from this experiment are presented in Table 19.

When the additives were applied to the moist soil, no

Table 19. Effect of organic additives on exchangeable K in the Marshall subsoil, when added to moist or oven-dry samples and when added to moist samples before drying at 110° C. for 48 hours in a gravity-draft oven

Additive	Exchangeable K (ppm.)			
	Added to undried soil		Added to oven-dry soil	
	undried	oven-dried	no H ₂ O	H ₂ O added
none	30	213	213	
water 7 ml.	30	196	--	114
sucrose 0.007 moles	31	28	--	112
cyclohexanol 7 ml.	30	26	147	112
n-octanol 3 ml.	--	24	--	108
glycerol 7 ml.	27	26	198	108

effect on extraction was apparent with the possible exception of glycerol. The additives applied to oven-dried soil should give a better test of their effect on extraction as they would be adsorbed on the soil to a considerable extent before the water was added. Conditions would therefore be quite similar to those pertaining where the additives had been applied before drying. The larger exchangeable K values in dried soils should also provide bigger differences between treatments which would be easier to measure. Glycerol and cyclohexanol added to the dry soil resulted in lower exchangeable K values than when no additive was applied. This is believed to have been caused by reversion due to water present in the chemicals.

This reversion would not be distinguishable from any effect the additives might have on extraction. It was to overcome this problem that water was added and the samples left moist for 8 hours.

The data in Table 19 show that the additives applied to the dried soil with water produced exchangeable K values below 210 ppm. due to reversion on re-wetting with water. Since addition of organic compounds with water resulted in the same amount of reversion as water alone, it is concluded that these additives had no important effect on extraction of K or on moist reversion. If the additives had affected either extraction or reversion, the exchangeable K would have been different than that obtained where only water was added.

These data also show that release of K occurs on drying and not on re-wetting. If release occurred on re-wetting application of additives after drying and before adding water should have prevented release as effectively as addition before drying.

DRYING MIDWESTERN SOILS WITHOUT RELEASE OF POTASSIUM

It has been shown that organic additives can be used to completely prevent the release of K normally occurring when the Marshall subsoil is dried. It remains to be determined whether K release can be prevented in other Midwestern soils.

Twenty moist samples were selected from K field experiments run in 1958 in the North Central Region of the United States. Most of these soils were chosen because of their known ability to release K on drying, but four were included that fix K on drying and three that show little change. Eleven of the samples were from the surface and nine from the 18 to 24 inch depth within the profile.

The effect of dextrose additions on exchangeable K have been shown to be largely independent of drying rate and amount of water present, factors which affect the exchangeable K values resulting from application of some of the other additives that have been tested. For this reason dextrose was used in an effort to control release of K on drying in these 20 soils.

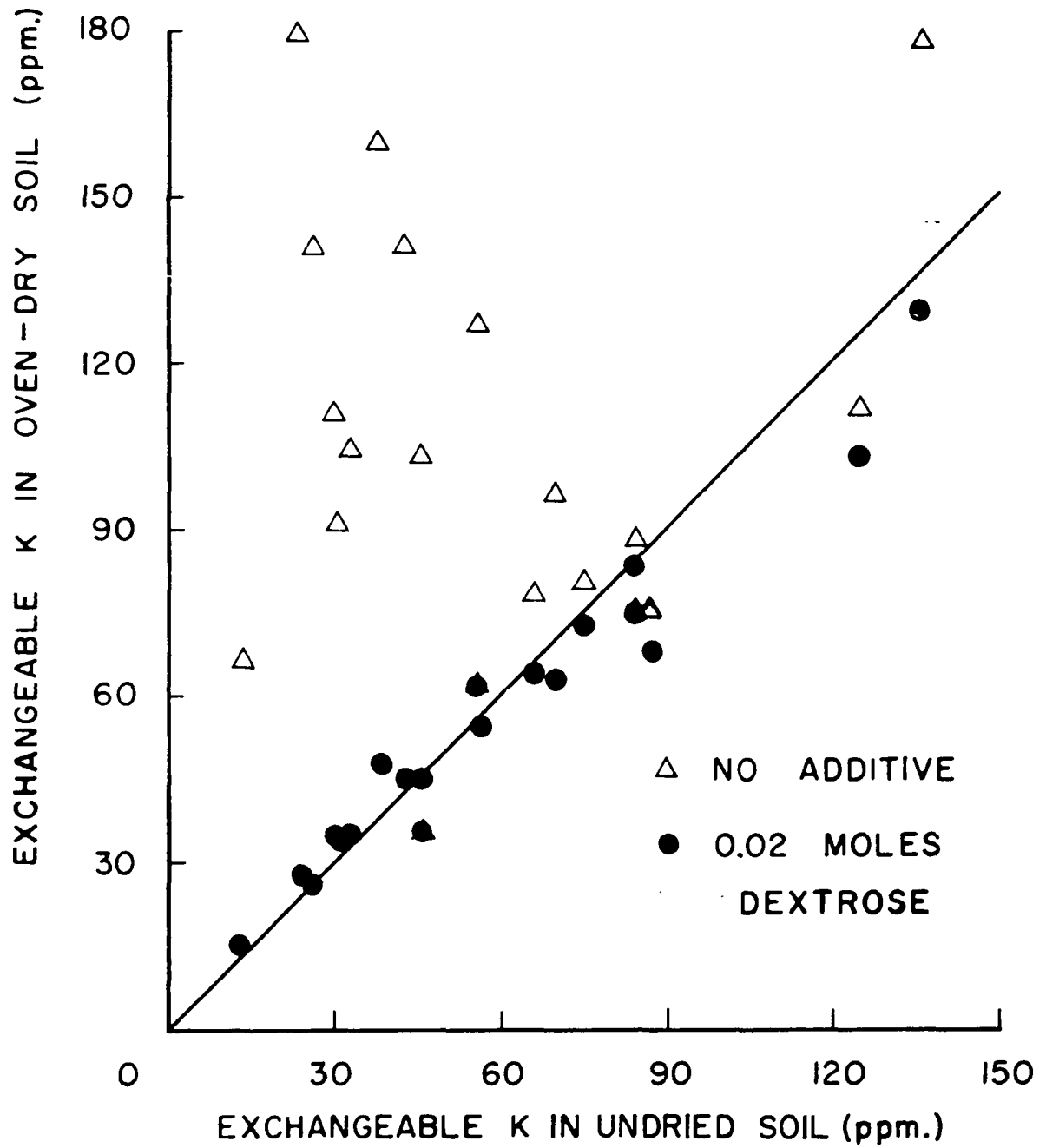
Ten-gram samples of moist soil were placed in 50 ml. beakers, 10 ml. of 2 M dextrose solution was added to each and the samples were dried at 110° C. for 48 hours in a forced-draft oven. Ten-gram samples of moist soil were also dried at 110° C. for 48 hours in a forced-draft oven without addition of dextrose. Moisture content was determined on these

untreated dried samples and exchangeable K was determined on both groups of dried samples as well as on the moist soils. All exchangeable K values were expressed as ppm. on an oven-dry soil basis.

In Figure 11 the exchangeable K values obtained with the oven-dried soil, with and without dextrose additions, are plotted against the exchangeable K values obtained with the moist soil. The figure has been separated into two parts by a line that represents the situation where the exchangeable K does not change on drying. Data falling above and to the left of this line represent soils whose exchangeable K value was higher in the dried soil than in the moist (K releasing soils). Data falling below and to the right of the line represent soils that fixed K on drying.

From the exchangeable K values plotted in the figure it can be seen that only four of the soils did not release K, on drying without addition of dextrose. Treatment with dextrose before drying quite effectively prevented release of K from all other soils so that the exchangeable K values obtained after drying with dextrose are very similar to those of the moist soils. Four soils fixed K on drying. Dextrose treatment before drying did not affect the amount of K fixed by two of these soils, but increased fixation in the other two. This treatment is therefore not effective in preventing fixation of exchangeable K on drying.

Figure 11. Exchangeable K values for twenty undried
Midwestern soils plotted against exchangeable
K values for the same soils after drying at
110° C. for 48 hours in a forced-draft oven
with and without prior addition of dextrose



It is evident that release of K was effectively blocked by addition of dextrose before drying in a number of Midwestern soils. Thus, one of the objectives of these studies has been achieved.

The effects developed with the Marshall subsoil are thus generally applicable to other soils that release K on drying. However, the data draw attention to another problem which arises in trying to obtain exchangeable K values from dried soils which are the same as those from moist soils. Some soils fix K on drying so that exchangeable K values will decrease. Organic additions before drying did not stop this change.

POTASSIUM RELEASE WITH TIME AND TEMPERATURE OF HEATING

It has been shown (Figure 2) that K can be released on drying at room temperature, but that more is released on drying at 110° C. Heat is usually used for drying soils, but little has been done to determine whether the release observed on drying is due to loss of water or whether some of it is due to temperature independent of water loss. Burns and Barber (1960) have concluded that temperature has a significant effect on K release independent of moisture loss. Further study on this question would appear to be of value. Studies presented thus far have been with drying at 110° C. and it would appear that investigations at higher temperatures might also provide useful information on K release.

Heating at 110° C. for Different Periods of Time

An experiment was conducted to determine whether K release on drying at 110° is entirely due to loss of water. Samples of Marshall subsoil were heated in a gravity-draft oven with the moisture allowed to evaporate (dry heating) and in an autoclave where the soil was kept moist by heating under steam pressure (moist heating). Preliminary experiments had shown that the effectiveness of additives in preventing K release was somewhat dependent on drying time. Additives were, therefore, included in these studies to determine their effect over longer periods of time. Sodium is a common

monovalent ion in the soil and is not usually believed to be fixed by lattice collapse. Exchangeable Na was therefore measured in the NH_4Ac extracts along with K to determine if moist or dry release was restricted to fixable ions.

Dry heating was conducted in a gravity-draft oven. Ten-gram samples of Marshall subsoil in 50 ml. beakers were placed in the oven at 110°C . They were removed, cooled and analyzed at various time intervals up to 40 days. Cyclohexanol at the rate of 7 ml. per 10 g. of soil was added to another group of samples which were dried at the same time. Previous observations have shown that when untreated samples were heated in the same oven as those treated with organic compounds such as cyclohexanol or octanol, the untreated samples did not always release as much K as if heated alone. It is believed that this occurred because those compounds which were effective in blocking release and have an appreciable vapour pressure were adsorbed to some extent on the untreated samples from the vapour in the oven. The cyclohexanol treated samples were therefore heated in a separate oven from the untreated samples for the first 72 hours of the heating period.

Moist heating was carried out in an autoclave at a temperature of 110°C . Samples were placed in platinum crucibles to eliminate any possibility of Na or K contamination from, or adsorption by, the glassware. Uncovered samples heated in the autoclave for longer time intervals lost

moisture. This was prevented in this experiment by placing the platinum crucibles inside tightly closed glass "Mason" jars along with a small amount of water. Four ml. of water was also added to each sample. The loss of water from samples in the autoclave appeared to occur when the autoclave was cooled and opened to add or remove samples. Therefore placement of samples in the autoclave was scheduled so that it was never opened more than three times while any one sample was in it. Half of the samples had 7 ml. of glycerol added as well as 4 ml. of water before heating and these were placed in separate "Mason" jars along with a small amount of water and glycerol.

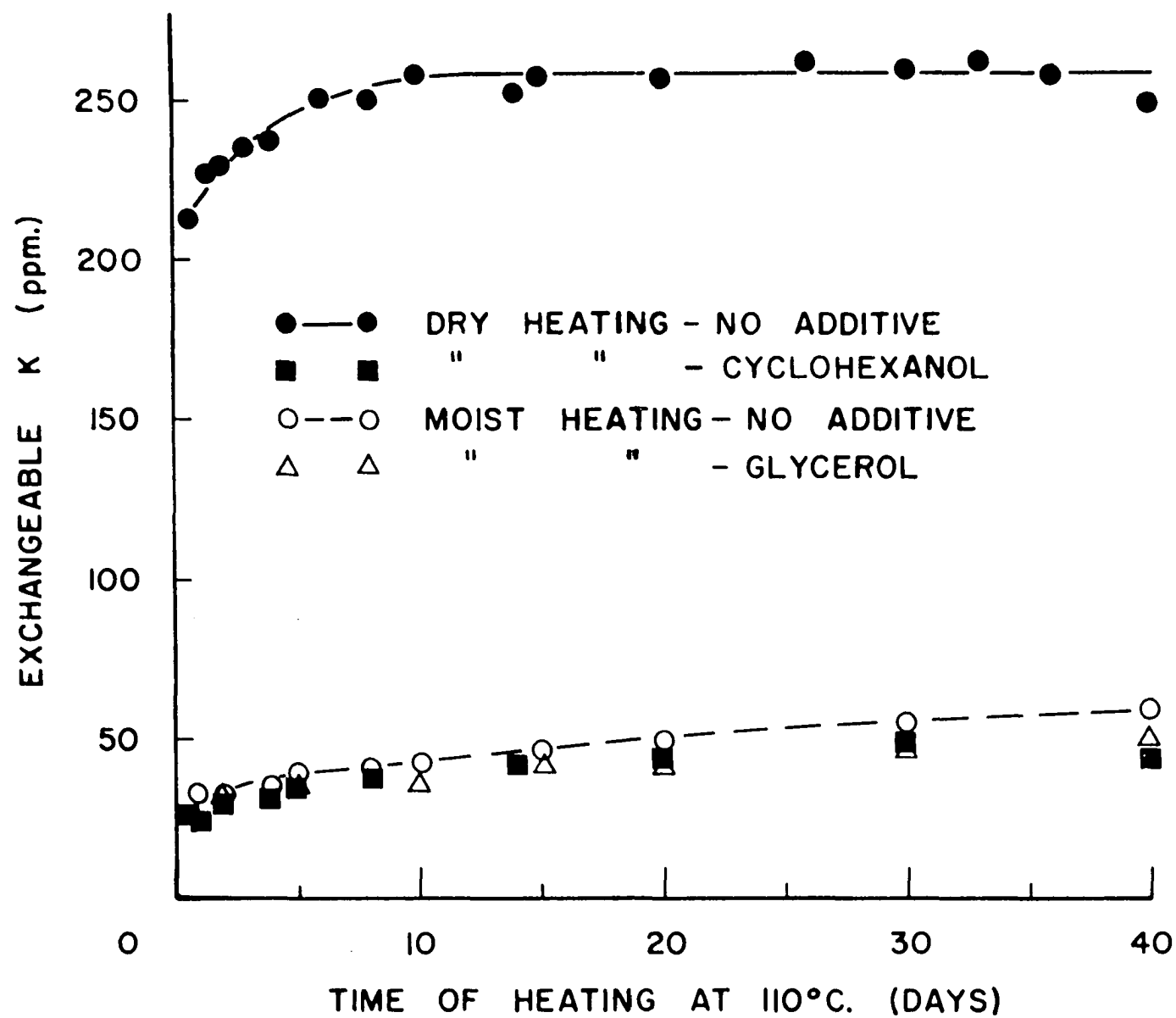
Cyclohexanol was used as the additive on samples heated in the oven as it has been shown to completely block release after 48 hours drying, at the rate used, and little of it remains on the sample for longer periods of heating (Table 18). Cyclohexanol was not used as the additive on samples heated moist, on the other hand, because the low solubility of cyclohexanol in water made it difficult to determine K on the flame photometer. Glycerol on the other hand is difficult to work with in the dry heated samples since it affects K readings on the flame photometer and, therefore, must be added to K standards used. It evaporates slowly from the dry heated samples but to correct the K readings on the flame photometer it is necessary to know the amount of glycerol present at the

end of each heating period. On heating in the autoclave, loss of glycerol was prevented, thus the amount of glycerol present was the same after each time interval. Glycerol was, therefore, used in preference to cyclohexanol for samples heated in the autoclave. The exchangeable K values for these experiments are presented in Figure 12.

On heating in the oven with no additive, it is apparent that most of the release on drying occurred in the first few hours. By the end of the first 48 hours the rate of release was much slower and by the end of 15 days it appeared to have ceased or decreased to a very low level. Heating in the autoclave without additive resulted in a very small amount of release compared with dry heating. Release was still continuing, but at a very slow rate, at the end of 40 days. The total K released during 40 days of moist heating was approximately 35 ppm. compared with 235 ppm. on dry heating. Therefore, that portion of the release on drying at 110° C. which is due to temperature alone, and not due to water loss, appears to be quite small.

It is interesting that dry heating with cyclohexanol gave very similar release patterns to moist heating without any additive. It can be concluded that addition of cyclohexanol limits K release to that which is a result of temperature alone and eliminates that release due to drying. Addition of glycerol reduced the amount of K released during moist heating

Figure 12. Exchangeable K in Marshall subsoil as affected by time of heating at 110° with and without drying and organic additions



only to a small extent. From evidence presented previously, it appeared that most of the cyclohexanol had been lost at the end of 48 hours of drying at 110° C. It seems highly unlikely that any significant amount of cyclohexanol remained on the soil after heating for 40 days. Thus, the data presented in Figure 12 may be taken as further evidence that to block the K release that occurs on drying, the additive need only be present until the water has been driven off.

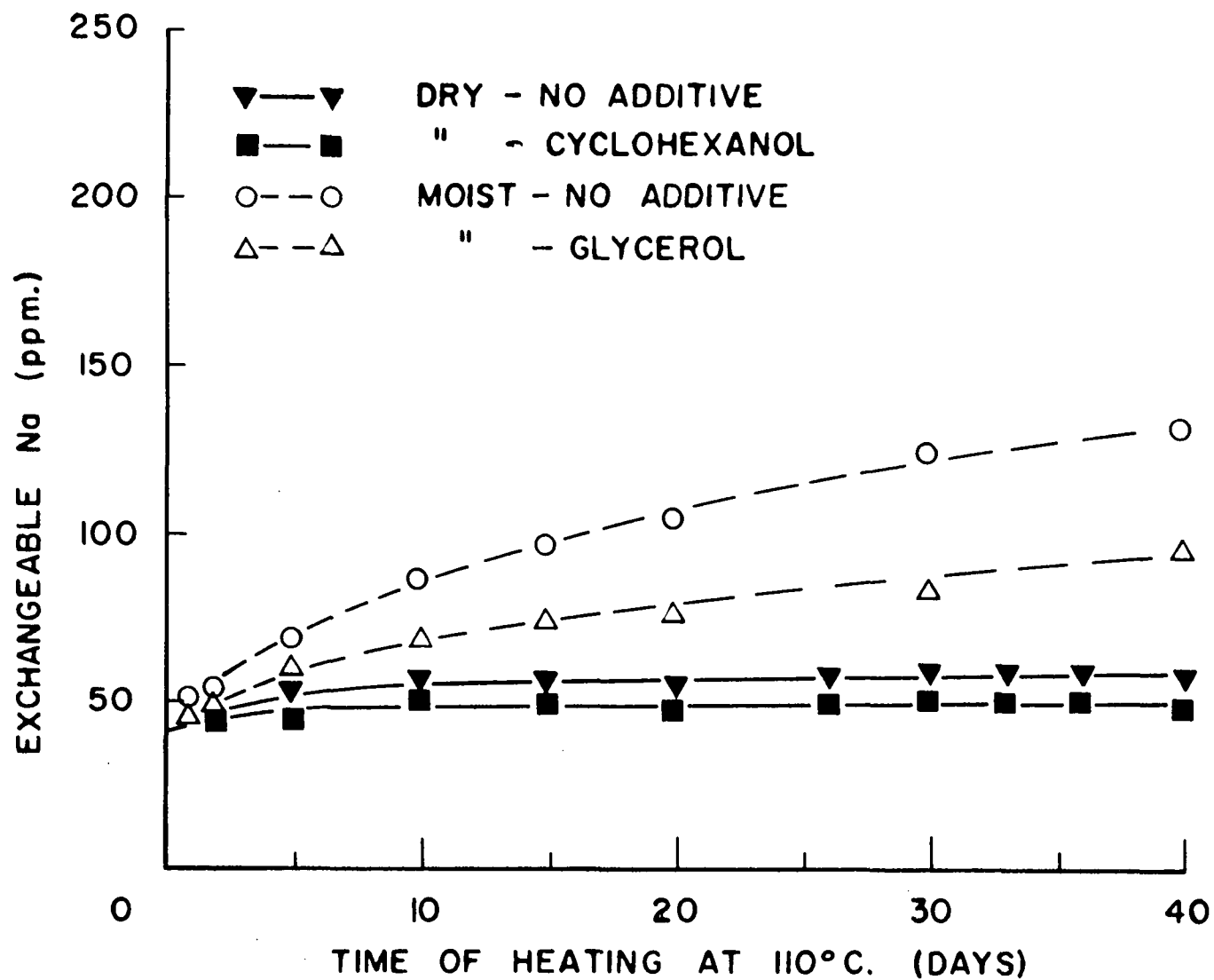
The exchangeable Na data for these same experiments have been presented in Figure 13. A very small amount of Na appears to have been released by heating in the oven and addition of cyclohexanol has almost completely blocked this release. Thus, Na release on drying behaves like K release, but is much more limited in extent. It may be that a small amount of Na is held in the lattice, collapsed with K, and that when K is released the Na becomes exchangeable as well.

The amount of Na released on moist heating is much greater than that released on dry heating and much greater than the amount of K released on moist heating. This release is approximately halved by the presence of glycerol.

Drying at Higher Temperatures

Scott et al. (1957) have shown that the Fayette and Carrington soils continue to release K on heating to temperatures above 110° C. Potassium release per unit of weight lost

Figure 13. Exchangeable Na in Marshall subsoil as affected by time of heating at 110° C. with and without drying and organic additions

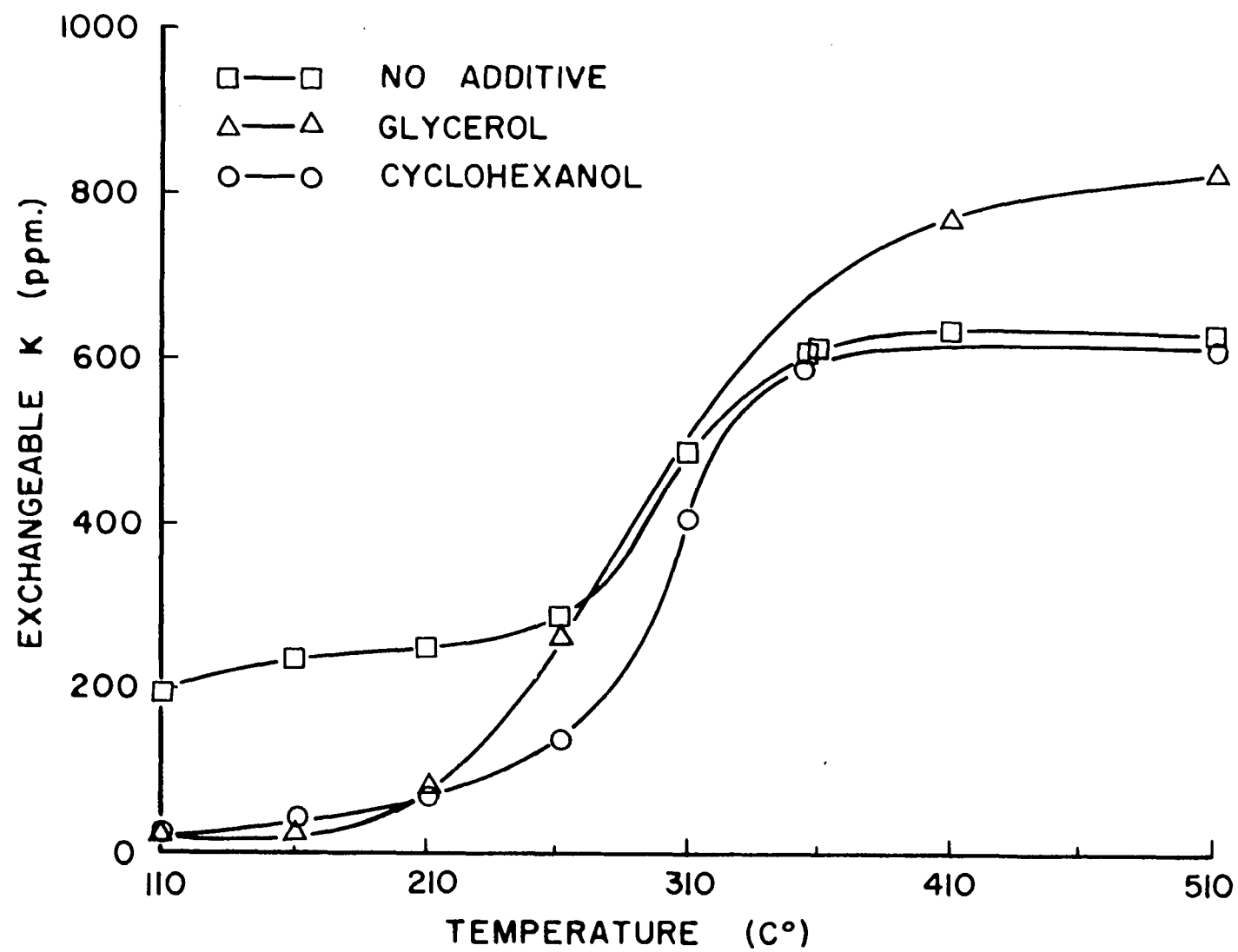


continued to increase up to 350° C. It was therefore decided to study K release from the Marshall subsoil at temperatures above 110° C. with and without the addition of organic compounds.

An experiment was conducted with no additive, with glycerol, and with cyclohexanol added to the moist Marshall subsoil before drying at temperatures from 110° to 510° C. All samples were heated at 110° C. for 48 hours. Those treatments to be heated at higher temperatures were then heated at the designated temperature for 48 hours. All heating at temperatures below 310° C. was carried out in a gravity-draft oven. Heating at temperatures of 310° C. and above was carried out in a muffle furnace. The furnace temperature fluctuated over a range of approximately 40° C. The furnace controls were therefore set so that the desired temperatures were at the top of the range. Thus, samples described as being heated at 310° C. were heated over a range of approximately 270° C. to 310° C. The changes of temperature in the furnace were sufficiently slow that the samples would have reached this maximum temperature each time the furnace temperature rose. Data from this experiment are presented in Figure 14. For temperatures above 310° C. the data represent only one determination.

Where no additive was applied the exchangeable K increased linearly with temperature from 110° C. to 260° C.

Figure 14. Exchangeable K in Marshall subsoil as affected by temperature of heating with and without organic additives



At temperatures between 110° C. and 200° C. the rate of release appears to be very similar to that obtained by Scott et al. (1957) with the Fayette and Carrington soils. There appears to be a sharp rise in exchangeable K between 280° C. and 310° C., but the rate of release levelled off again at approximately 260° C. This sharp increase in exchangeable K does not appear to coincide with water loss from any of the clay minerals except vermiculite. Grim (p. 231, 1953) mentions an endothermic reaction due to loss of interlayer water from vermiculite at 250 to 275° C. When vermiculite is heated abruptly to 300° C., it exfoliates. Water loss from natural vermiculite occurs at 250 to 275° C., but K vermiculite shows no such peak and it is therefore doubtful if K release could be attributed to this source. The release of K at 270 to 310° C. does coincide with oxidation of organic matter and may be related to this. There is no assurance, however, that release of K at these elevated temperatures is due to the same causes as release at 110° C. and below.

Between 110 and 160° C., release of K with cyclohexanol added is at approximately the same rate as without, although the level of exchangeable K is much lower. Release begins to increase rapidly at a slightly lower temperature with cyclohexanol than without it so that the two curves approach each other at 360° C.

In presence of glycerol K release does not occur between

110 and 160° C. but increases rapidly with temperature above 160° C. Exchangeable K in the glycerol treatment exceeds that in the treatment with no additive for all temperatures above 280° C.

The vapour pressure or boiling point of glycerol and cyclohexanol appear to have little relation to their effect on release of K above 110° C. In presence of cyclohexanol the exchangeable K begins to rise rapidly at approximately 270° C., considerably above the boiling point of cyclohexanol (162° C.). If, as has been suggested earlier, cyclohexanol is largely lost in the 48 hours of heating at 110° C., its vapour would not be expected to affect the shape of the curve. Glycerol (B.P. 290° C.) is known to be present after drying at 110° C. and loss of glycerol could conceivably cause the increase in K release beginning at 210° C. It is difficult, however, to understand why the exchangeable K on the glycerol treatment should continue to increase above that of the treatment with no additive. Better heat control is required for study of K release in this temperature range.

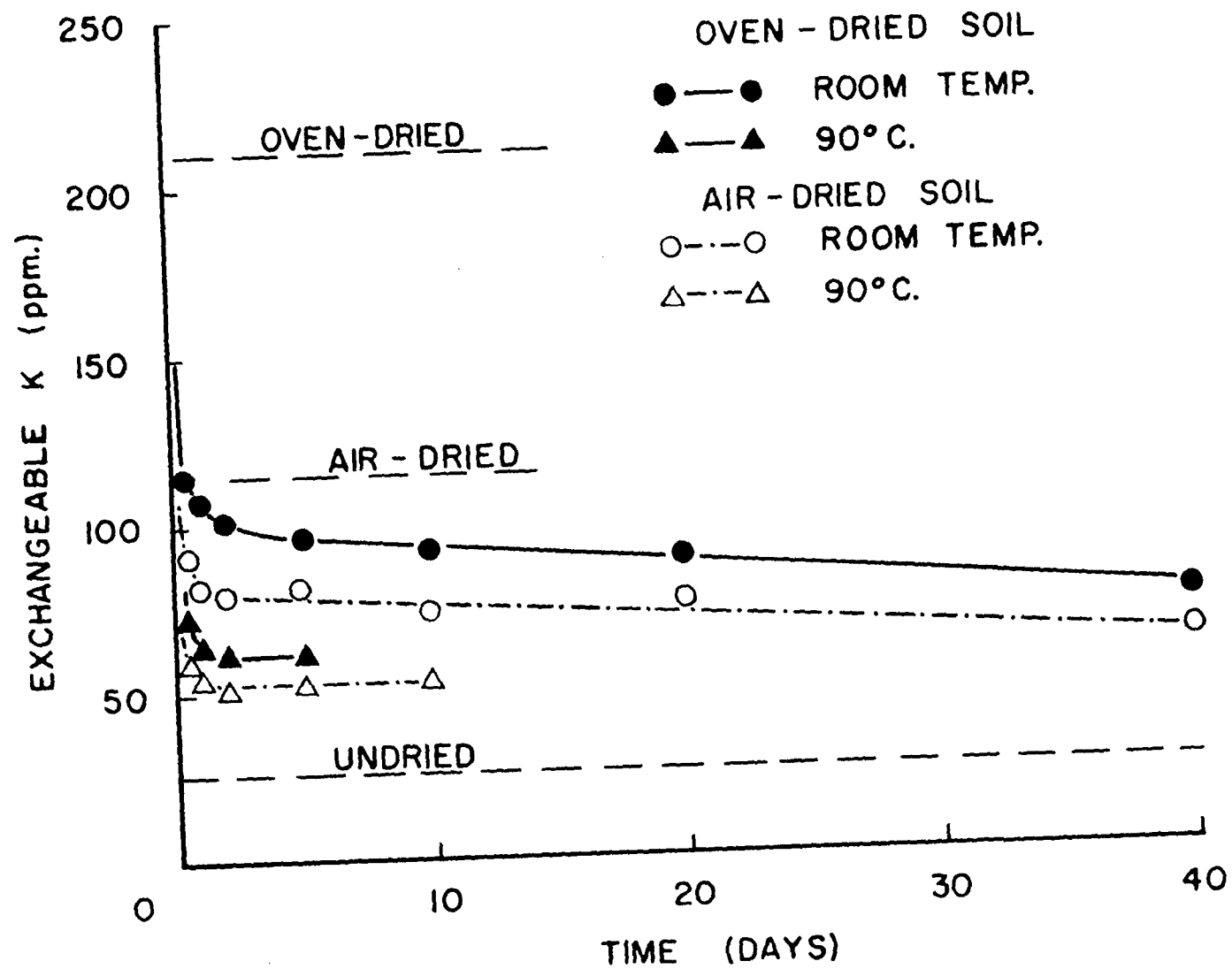
MOIST REVERSION OF POTASSIUM IN THE MARSHALL SUBSOIL

When oven-dry soils are re-wet with water some of the K that was released by drying reverts to a non-exchangeable form. It has been shown by Hanway et al. (1960), however, that re-wetting of dried samples does not lead to complete reversion of the K released on drying in any one soil nor does it lead to consistent amounts or percentages of reversion with different soils. One of the objectives of this study was to find a method of treating dried soils so that the exchangeable K extracted would be the same as that extracted from undried soils.

Moist reversion of K in Marshall subsoil was studied at room temperature and at 90° C. Reversion studies at room temperature were carried out by placing 10 g. samples of air and oven-dry soil at 125 ml. Erlenmeyer flasks with 7 ml. of water and covering with Al foil. The samples were left at room temperature for the prescribed period of time and were then extracted with NH_4Ac . Reversion studies at 90° C. were carried out by placing 10 g. samples of air and oven-dry soil in 50 ml. round bottom flasks heated in a water bath with air condensers on the flasks to reduce evaporation. Water was periodically added, to those samples heated for longer periods, to compensate for that lost by evaporation. Data from this experiment are presented in Figure 15.

Reduction in exchangeable K in the oven-dried soil after

Figure 15. Exchangeable K in air and oven-dried Marshall subsoil after addition of water and storage at 25 and 90° C. for different periods of time



re-wetting at room temperature occurred very rapidly at first, but became slower with time. During the period from 5 to 40 days the exchangeable K was decreasing at a constant rate of less than 2 ppm. per day. Moist reversion of K in the oven-dried soil at 90° C. had proceeded considerably further at the end of 12 hours than reversion at room temperature. It appeared to have ceased at the end of two days at a level considerably lower than that attained at room temperature, even after 40 days. Moist reversion of air-dried soils follows similar patterns, but with the exchangeable K levels being somewhat lower than with oven-dried soils. It is interesting to note that, although on re-wetting air-dried soils result in lower exchangeable K values than oven-dried, the actual amount of reversion is less in the air-dried soils as they were much lower in exchangeable K to start with. The lowest exchangeable K value obtained after reversion in this experiment was 53 ppm. compared with 27 ppm. of exchangeable K for the undried soil. It appears that the degree of reversion attained, after re-wetting a dried soil, depends on the degree of drying. The temperature of moist incubation is important in determining the rate of reversion.

THE EFFECT OF ORGANIC ADDITIVES ON POTASSIUM REVERSION

Organic additives were shown to be quite effective in blocking the release of K in soils on drying. With studies using dextrose to block release of K in a group of Mid-western soils, it was noted that two soils which fixed K on drying fixed more on drying with dextrose than without it. Heating of the undried Marshall subsoil in presence of ethanol also resulted in some slight fixation of K (Table 17). Thus, in certain cases organic additives have resulted in more fixation of K than where no additive was present. It was, therefore, decided to study their effects on reversion.

Organic Compounds with Water and Drying

A group of the organic compounds which had proved most effective in blocking K release were added to samples of oven-dry Marshall subsoil and left for one hour to determine their effect on reversion of K. Data from this experiment are presented in Table 20.

Addition of water resulted in greater reversion than any of the compounds tested, reducing the exchangeable K from 210 ppm. to 116 ppm. Sucrose in water produced identical results suggesting that sucrose itself had no effect on reversion. Glycerol and cyclohexanol additions resulted in some decrease in exchangeable K. In view of the large effect of water on reversion, however, it is considered probable that these

Table 20. Exchangeable K in oven-dried Marshall subsoil one hour after addition of water or organic materials

Treatment	Exchangeable K (ppm.)
none	210
water - 7 ml.	116
glycerol - 7 ml.	198
cyclohexanol - 7 ml.	147
sucrose - 7 ml. of 1 M in H ₂ O	116

effects were due to water present in the chemicals added.

Since the effects of several compounds on K reversion was believed to be confounded by presence of water, it was decided to study the relative effects of these compounds on K reversion when added with uniform amounts of water. Glycerol, cyclohexanol, sucrose and n-octanol were added to oven-dry samples of Marshall subsoil followed by 7 ml. of water. The samples were stirred gently and left at room temperature for eight hours. Half of them were then extracted with NH₄Ac and the other half were dried at 110° C. for 48 hours before extraction. Data from this experiment are presented in Table 21.

Approximately the same amount of reversion occurred when water was added to the samples alone as when water was added with organic additives. From this it is concluded that these

Table 21. Exchangeable K in oven-dried Marshall subsoil as affected by addition of organic compounds and water followed by re-drying

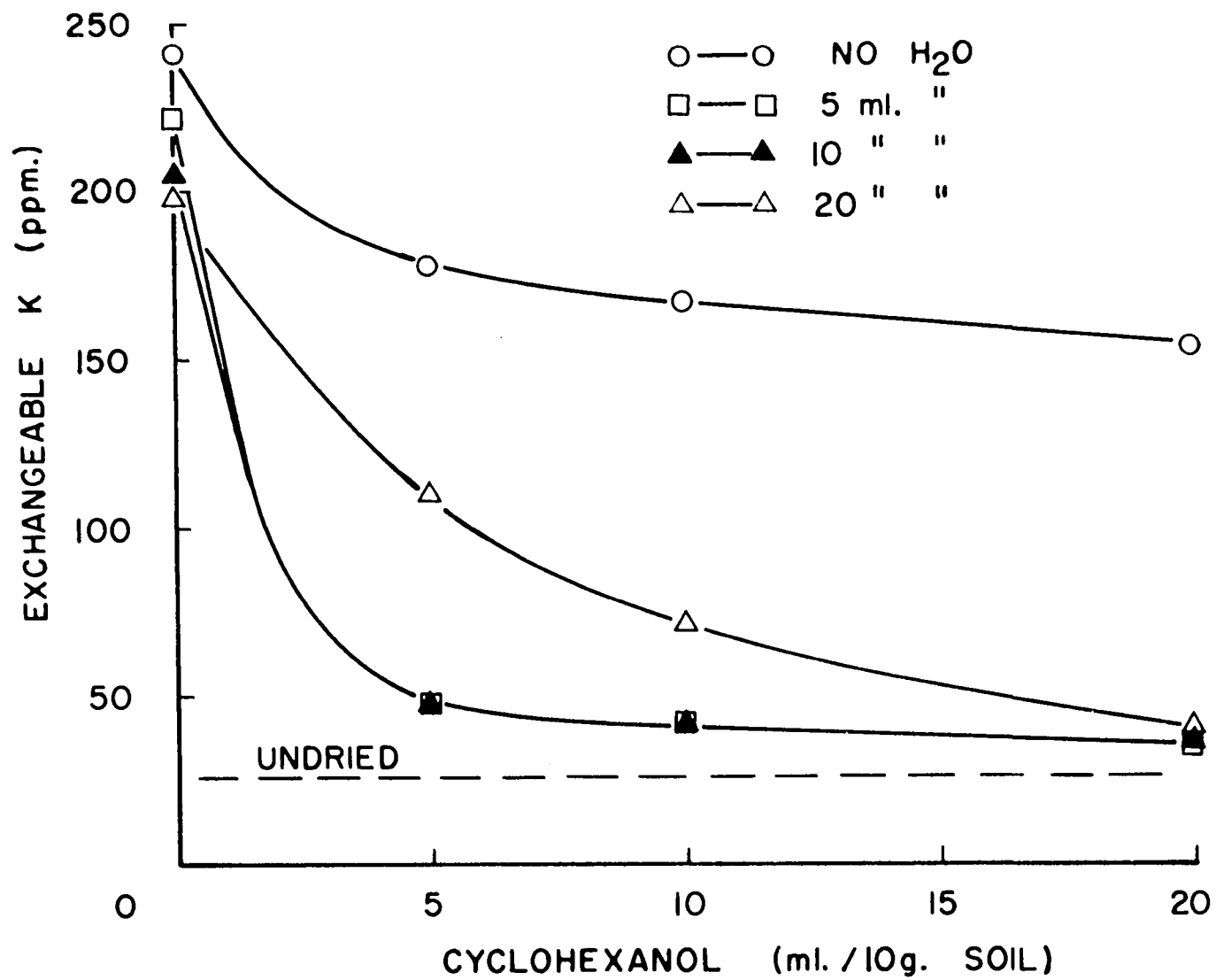
Treatment	Exchangeable K (ppm.)	
	undried	oven-dried
none	210	--
14 ml. H ₂ O	114	218
7 ml. H ₂ O + 7 ml. glycerol	108	54
7 ml. H ₂ O + 7 ml. cyclohexanol	112	48
7 ml. H ₂ O + 7 ml. 1 M sucrose	112	63
7 ml. H ₂ O + 3 ml. n-octanol	108	--

organic additives do not affect reversion of K at room temperature.

When the samples were re-dried, after addition of organic compounds and water, considerable reversion occurred. Addition of cyclohexanol and re-drying, for example, reduced exchangeable K from 210 to 48 ppm.

Since addition of organic compounds and water followed by drying was shown to cause reversion of K, it became of interest to determine in what combinations and at what rates they were most effective. An experiment was therefore conducted in which cyclohexanol and water in various combinations were added to oven-dry Marshall subsoil before re-drying at 110° C. for 48 hours in a gravity-draft oven. Data from this experiment have been plotted in Figure 16.

Figure 16. Exchangeable K in oven-dried Marshall subsoil as affected by cyclohexanol and water additions followed by re-drying at 110° C.



Where no water was added, cyclohexanol caused a certain amount of reduction in the amount of exchangeable K extracted after re-drying. Larger additions of cyclohexanol reduced the exchangeable K further. A similar reduction was observed where cyclohexanol was added without re-drying (Table 20). It is suggested that in both of these cases the reduction in exchangeable K was due to water present in the cyclohexanol. It is further suggested that no appreciable reversion occurs either on addition of, or re-drying with, organic compounds unless water is present. When 5 or 10 ml. of water were added to each 10 g. of soil, cyclohexanol was quite effective in reducing the exchangeable K, but was less efficient when 20 ml. of water was added. It is evident that some water must be added to get large effects on K reversion with organic additives, but large additions of water reduce reversion.

When water and an organic compound are added to an oven-dry soil and the soil is re-dried, it is suggested that the organic compound prevents release of K, by whatever mechanism release occurs on drying. Fixation of the K previously released is believed to occur by collapse of the clay mineral lattice as the water is driven off. It appears that release and fixation of K may occur simultaneously when a soil is dried. The organic additives appear to block release on drying, but not fixation. Thus, while the net result of cyclohexanol addition is an increase in reversion, it is suggested

that the additive only blocks release so that the reversion which occurs is more apparent.

If the role of the cyclohexanol is simply to prevent release of K on drying the lower efficiency at higher rates of water could be expected from observations in a previous section. It was shown in Figure 16 that additions of water reduced the effectiveness of cyclohexanol in blocking release of K, and it was suggested that the organic additive must be present until all the water has been driven off to completely block release. Thus, addition of more water makes it necessary for more of the organic compound to be added, if it is volatile, in order that some will remain until after the water has evaporated.

The data presented in Figure 16 show that cyclohexanol applications, even at the 20 ml. rate, did not lead to complete reversion of the K released on drying, since the exchangeable K did not drop to the original level in the moist soil (27 ppm.). It appeared possible that other organic additives might be more effective.

Rates of Addition of Organic Compounds

Studies on reversion with organic compounds reported thus far have been carried out using some of the compounds which proved to be effective in blocking K release. With the rates and methods of application used, none of these compounds

produced complete reversion of the K released on drying. It appeared that further work was required to find what compounds are most effective in causing reversion.

A number of compounds were added to 10 g. samples of oven-dry Marshall subsoil along with 7 ml. of water. All treatments were then re-dried at 110° C. for 48 hours in a gravity-draft oven and exchangeable K was determined. Data from these treatments are presented in Table 22.

From a comparison of the data in Table 22 with those in Table 10, it is apparent that not all compounds which were effective in blocking K release are effective in causing reversion. Cyclopentanone, at the rates used, was reasonably effective in stopping K release, but was rather ineffective in causing reversion. Glycerol and sucrose were among the most effective compounds in blocking K release, but were not the most effective in causing reversion. The normal alcohols, n-hexanol and n-octanol, appeared to be the most effective compounds tested in causing reversion. These compounds were believed to merit further study particularly in regard to rates of addition.

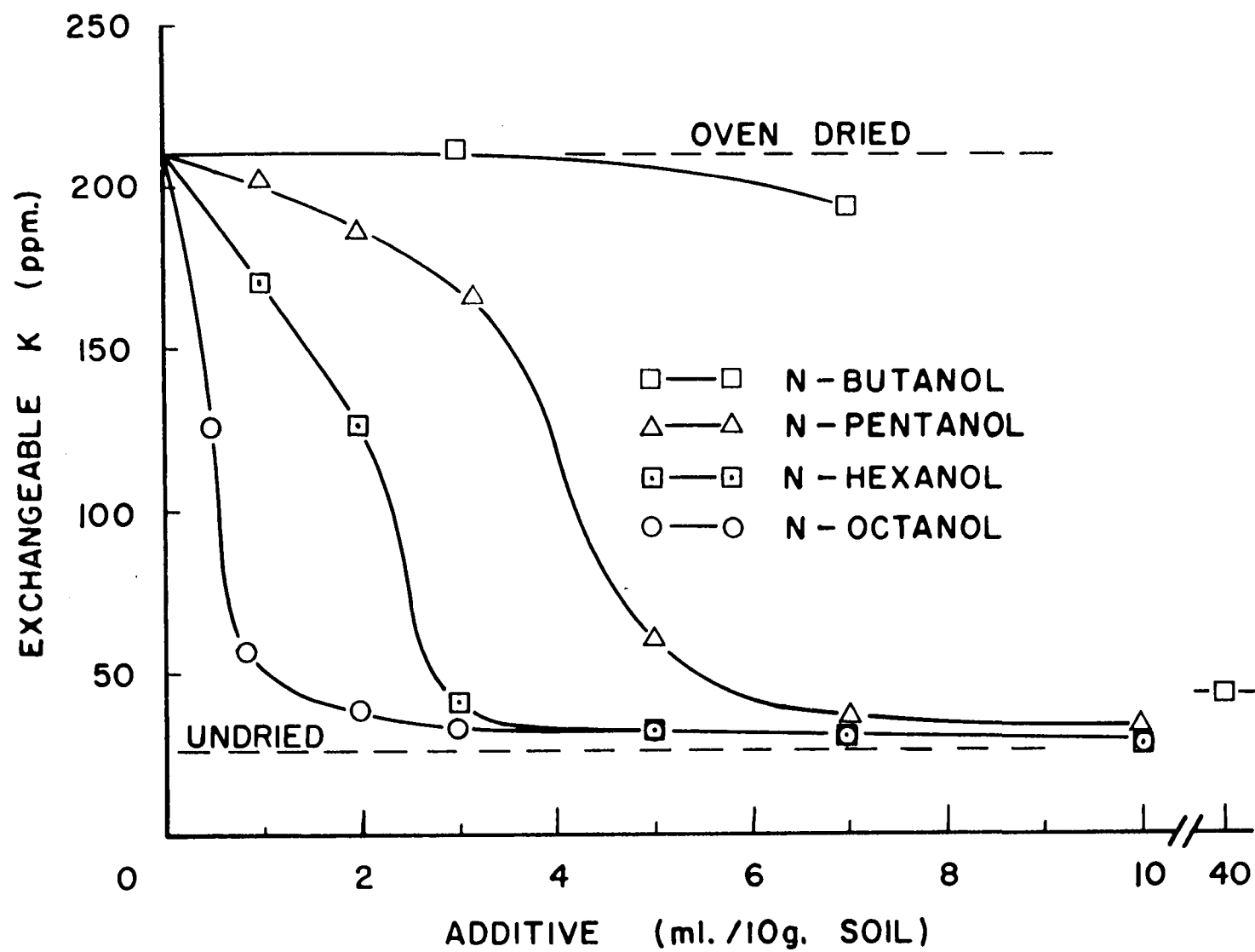
Several straight chain alcohols were added at varied rates to 10 g. samples of oven-dry Marshall subsoil along with 7 ml. of water. The samples were then re-dried at 110° C. for 48 hours in a gravity-draft oven. Data from this experiment are plotted in Figure 17.

Table 22. Exchangeable K in oven-dried Marshall subsoil as affected by addition of organic compounds and water followed by re-drying

Additive	Exchangeable K (ppm.) ^a	
	3 ml.	7 ml.
H ₂ O	--	210
n-butanol	212	194
n-hexanol	40	32
n-octanol	32	30
2-octanol	46	42
cyclohexanol	60	48
3-methyl cyclohexanol	44	38
cyclohexanone	--	70
cyclopentanone	--	186
2-2 dinethyl-1-pentanol	112	46
2-ethyl-1-hexanol	43	38
1-3 propanediol	--	82
glycerol	--	57
ethylene glycol	76	61
triethanolamine	--	77
sucrose 1 M	--	64
glycine 1 M	--	178
pyridine	--	94

^aThe undried soil contained 27 ppm. exchangeable K.

Figure 17. Exchangeable K in oven-dried Marshall subsoil as affected by addition of varied amounts of normal alcohols with 7 ml. of water followed by re-drying

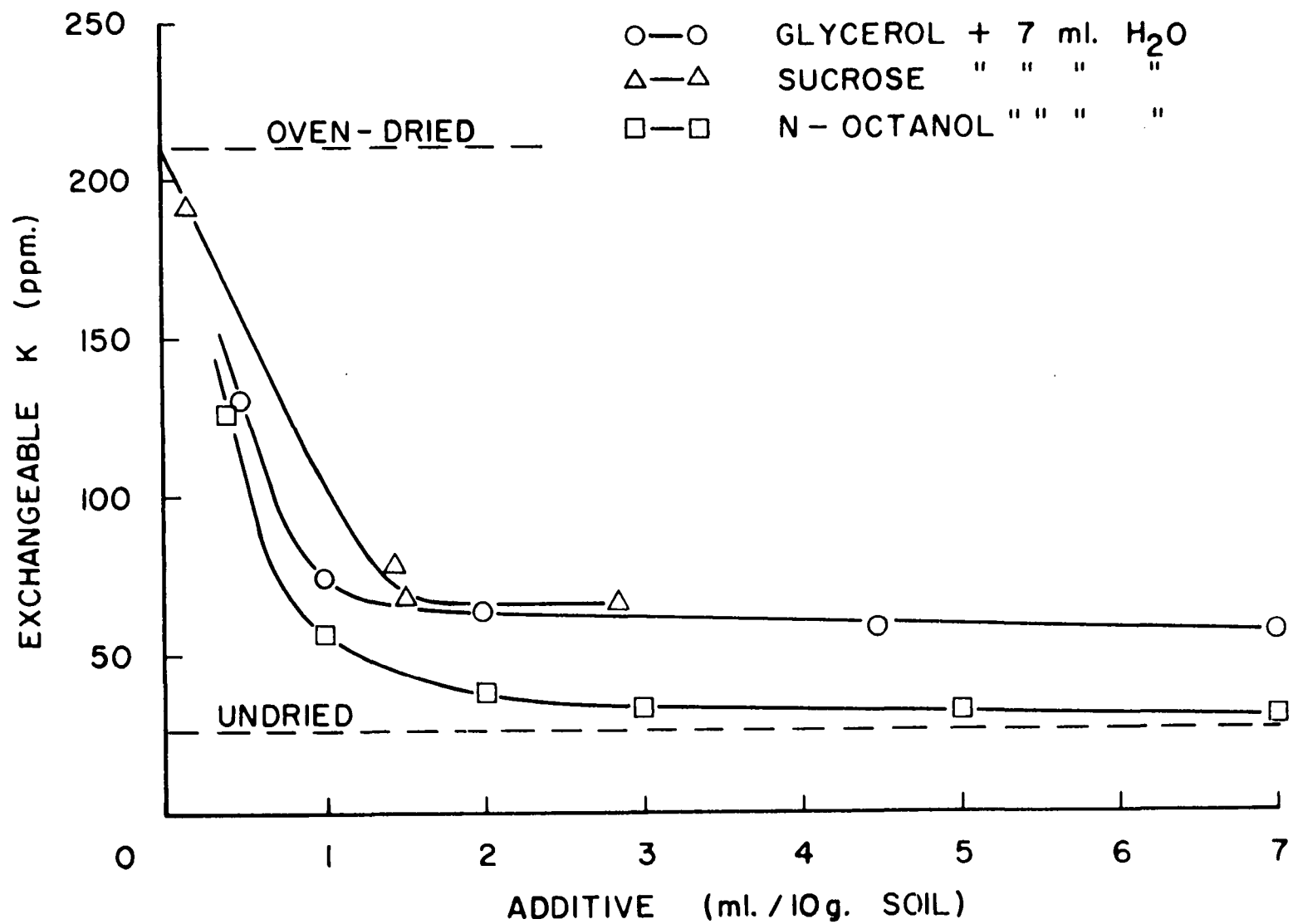


The curves obtained when exchangeable K is plotted against the amount of alcohol added are very similar to those for release studies (Figure 5). The volume of n-octanol and n-hexanol, 3 to 4 ml., required for maximum reversion of K was approximately the same as that required to block release completely. Both octanol and hexanol permitted reversion of K almost to the level in the undried soil. The more volatile alcohols, butanol and pentanol, however, were much less effective in causing reversion of K than they were in blocking release. This difference may be due to the fact that 7 ml. of water was added in reversion studies compared to a 2.2 ml. contained in the moist soil used in the release study.

Glycerol and sucrose, at the single rate tested, were shown in Table 22 to be less effective than hexanol or octanol. These compounds have been shown to be as effective as octanol in blocking release. To study this difference further, glycerol and sucrose were added to 10 g. samples of oven-dry Marshall subsoil along with 7 ml. of water. The samples were re-dried for 48 hours at 110° C. and the exchangeable K values obtained were compared with those for octanol. Data from this experiment are presented in Figure 18.

It is apparent that sucrose and glycerol are considerably less effective than octanol in permitting reversion of K. The release data plotted in Figure 9, however, show that sucrose and glycerol are as effective as octanol in blocking release

Figure 18. Exchangeable K in oven-dried Marshall subsoil as affected by addition of varied amounts of glycerol, sucrose and octanol with 7 ml. of water followed by re-drying



of K. In the reversion study, glycerol and sucrose additions, followed by drying, resulted in exchangeable K values of 58 and 66 ppm. respectively compared to 62 ppm. after moist heating with water (Figure 15). Thus, glycerol and sucrose were of no value for increasing reversion.

Upon re-wetting of an oven-dry soil, some of the K which has been released on drying is fixed. It appeared (Figure 15) that this reversion occurred in the Marshall subsoil to a minimum exchangeable K value of approximately 60 ppm. On re-drying with certain organic additives, further reversion of K occurred. With addition of glycerol and sucrose, which are not driven off on heating at 110° C., it appears that further reversion, beyond that occurring in the moist state, does not occur. It is suggested that glycerol and sucrose prevent this further reversion because they are adsorbed on interlayer positions of the clay mineral lattice and prevent its collapse. This would explain why glycerol and sucrose are less effective than the more volatile octanol in permitting reversion of K on re-drying.

If glycerol and sucrose are less effective in permitting reversion of K because they prevent collapse of the lattice, they should also prevent additional reversion from occurring when they are applied to soils along with additives which otherwise do allow more reversion to occur. To determine if this is true, sucrose and octanol were added separately and

together to 10 g. samples of oven-dry Marshall subsoil followed by addition of 7 ml. of water. The samples were then re-dried at 110° C. for 48 hours in a forced-draft oven. Data from this experiment are presented in Table 23.

Table 23. Exchangeable K in oven-dried Marshall subsoil as affected by addition of octanol and sucrose with water, followed by re-drying at 110° C. for 48 hours in a forced-draft oven

Additions	Exchangeable K (ppm.)
7 ml. H ₂ O	218
7 ml. of 1 M sucrose in H ₂ O	68
7 ml. of 1 M sucrose in H ₂ O + 7 ml. n-octanol	62
7 ml. of n-octanol + 7 ml. H ₂ O	41

Additions of sucrose with octanol resulted in exchangeable K values which were nearly as high as those with sucrose added alone, and considerably higher than those with octanol alone. This would support the conclusion that sucrose additions result in less reversion of K than more volatile additions because sucrose prevents collapse of the clay mineral lattice.

It is apparent from a comparison of the data presented in Table 23 and Figure 17 that the exchangeable K values resulting from octanol treatment are different in the two places. Data from Table 23 were obtained from re-drying in a forced-

draft oven, those in Figure 17 from re-drying in a gravity-draft oven. Forced-draft and gravity-draft ovens were directly compared in an experiment using octanol and sucrose as additives. Seven ml. of n-octanol with 7 ml. of water and 7 ml. of 1 N sucrose in water were added to 10 g. samples of oven-dry Marshall subsoil followed by heating at 110° C. for 48 hours. Data from this experiment are presented in Table 24.

Table 24. Exchangeable K in oven-dry Marshall subsoil as affected by organic additions with water followed by re-drying in gravity and forced-draft ovens at 110° C.

Additive	Drying oven	Exchangeable K (ppm.)
n-octanol	gravity-draft	30
"	forced-draft	41
sucrose	gravity-draft	66
"	forced-draft	68

The effect of sucrose was changed little by drying method, while the effect of octanol was changed considerably. The forced-draft oven apparently leads to less complete reversion of K with compounds which are volatile. It was also noted (Figure 16) that addition of excess water reduced the effectiveness of cyclohexanol in causing reversion. These effects are similar to those observed in release studies where forced-air drying or additions of water reduced the effective-

ness of organic compounds. From these observations in the release studies, the conclusion was reached that the organic additive only needed to be present on the soil while water was being driven off to be effective. Some of the least effective compounds became completely effective if they could be maintained on the soil while the water was lost. It would appear that a similar situation applies in regard to the effect of organic compounds on reversion.

It was decided to determine if reversion would occur when otherwise less effective compounds were maintained on the soil. Cyclohexanol was found to be only moderately effective in permitting reversion of K (Figure 16). An experiment was therefore set up in which cyclohexanol and 10 ml. of water were added to oven-dry Marshall subsoil and various heating treatments applied. Samples with and without cyclohexanol were placed in 50 ml. beakers which were placed in closed "Mason" jars and heated (moist) in an autoclave at 113° C. for 48 hours. Cyclohexanol treated samples were heated in separate jars. On removal from the autoclave one group of samples was extracted and the remainder were heated at 110° C. in a gravity-draft oven for varying periods of time. Cyclohexanol was maintained on some of the samples in the oven by addition of the hot liquid when required to keep the soil covered. Data from this experiment are presented in Table 25.

Complete reversion of K to the original moist value

Table 25. Exchangeable K in oven-dried Marshall subsoil as affected by addition of water and heating in presence of cyclohexanol

Treatment	Exchangeable K ^a (ppm.)
1. none	242
2. H ₂ O added, heated moist	66
3. H ₂ O added + 7 ml. cyclohexanol, heated moist	54
4. H ₂ O added + 7 ml. cyclohexanol, heated moist, then heated 48 hours in oven with cyclohexanol	28
5. as treatment 4, but heated a further 48 hours without cyclohexanol	36

^aUndried soil contained 27 ppm. exchangeable K.

occurred when cyclohexanol was maintained on the sample and the water was allowed to evaporate. This agrees with findings in release studies that the additive need only be maintained on the sample to be completely effective. Where further heating was carried out, with the cyclohexanol allowed to go off, a certain amount of K was released again.

Ethanol had even less effect on reversion than cyclohexanol when simply added to the oven-dry soil with water and re-dried. Therefore, as a further test of the concept presented above, ethanol was used in an experiment similar to that with cyclohexanol in order to determine if it would be more effective when maintained on the soil. Ethanol and 7 ml.

of water were added to oven-dry Marshall subsoil and heated at 75° C. for various periods of time in a gravity-draft oven. Ethanol was maintained on the soil by adding hot liquid as required. Thus water was driven off by heating in presence of ethanol as in the release experiment presented in Table 17. Data from this experiment are presented in Table 26.

Table 26. Exchangeable K in oven-dried Marshall subsoil as affected by addition of water and heating in presence of ethanol at 75° C. in a gravity-draft oven

Treatment	Exchangeable K ^a (ppm.)
Oven-dry soil	242
Heated 24 hrs. at 75° C. in presence of ethanol, allowed to dry 24 hrs. at 75° C.	76
Heated 48 hrs. at 75° C. in presence of ethanol	36

^aUndried soil contained 27 ppm. of exchangeable K.

In presence of ethanol the exchangeable K dropped to 36 ppm., considerably below that produced on heating at 90° C. in water. It is probable that further heating in presence of ethanol would have caused more complete reversion.

Complete reversion occurred with cyclohexanol and a considerable amount with ethanol when they were maintained on the soil. It appears that many of the compounds tested would permit complete reversion of the K released on drying if they

were maintained on the sample until all the water was lost. Sucrose and glycerol have the advantage that they are easy to maintain on the soil while H_2O is being lost but they do not permit complete reversion of K, apparently because they prevent collapse of the clay mineral lattice. It is suggested that cyclohexanol and ethanol are less tightly held on the clay mineral lattice than glycerol, sucrose or water. Thus, they would be less of a barrier to collapse of the clay mineral lattice and fixation of K. It has been found that cyclohexanol was less effective in causing reversion or in blocking release than other alcohols of similar boiling point and that its effectiveness was reduced more by water additions. These findings suggest that cyclohexanol is not strongly adsorbed by the clay mineral lattice.

Routine Methods for Maximum Reversion

The experiments just described with cyclohexanol and ethanol have shown that it is possible to obtain complete reversion by heating oven-dried soils for sufficient periods of time in the presence of organic materials. Such methods are not suitable, however, for routine use with large numbers of soil samples. For this purpose simpler techniques such as addition of an organic compound with water, followed by drying in the oven, would be more desirable. The addition of octanol and water to the soil followed by drying for 48

hours at 110° C. in a gravity-draft oven has resulted in more complete reversion of K than any other method tested thus far. However the number of samples that are dried in a gravity-draft oven at one time will affect the rate of loss of octanol from each sample, and any excess liquid octanol remaining after heating can cause difficulties in determination of K. The build-up of octanol vapour in the oven also creates a fire hazard. In the forced-draft oven, on the other hand, drying is so rapid that octanol is much less efficient and large additions are required to cause complete reversion of K. A steam hot-plate located in a fume hood appeared to be a reasonable compromise. It allows slower drying than in a forced-draft oven, thus making reversion more complete, but it provides sufficient circulation to prevent high concentrations of octanol from building up around the samples.

Two rates of octanol and cyclohexanol were added, with 7 ml. of water, to oven-dry Marshall subsoil in 50 ml. beakers. For one drying treatment the beakers were covered with Al foil and heated on a steam hot-plate for 48 hours after which they were uncovered and heated for a further 48 hours. In the second treatment the beakers were heated uncovered for 48 hours. Data from this experiment are presented in Table 27.

From the data presented it is apparent that octanol caused complete reversion at the 20 ml. rate with either

method of drying. At the 7 ml. rate neither drying treatment produced complete reversion, although reversion was greater where the samples were heated 48 hours covered before heating uncovered. Cyclohexanol was not as effective as octanol under either of the drying methods. It appears that a 20 ml. addition of octanol, with either of the drying methods tested, will produce complete reversion of the K released on oven-drying in the Marshall subsoil.

Table 27. Exchangeable K in oven-dried Marshall subsoil as affected by additions of octanol and cyclohexanol with water, followed by re-drying on a steam hot-plate

Additive	Exchangeable K (ppm.)	
	Beakers open, 48 hrs.	Beakers covered, 48 hrs. open, 48 hrs.
7 ml. n-octanol	36	32
20 ml. "	29	28
7 ml. cyclohexanol	47	44
20 ml. "	39	41

REVERSION OF POTASSIUM IN TWENTY MIDWESTERN SOILS

It was shown that the exchangeable K in the oven-dried Marshall subsoil could be lowered to that of the undried soil. It still remains to be shown whether or not the same thing can be accomplished with K releasing soils in general, and particularly by the simple method of adding octanol and drying on a steam hot-plate.

An experiment was conducted using air-dry samples from soils of the North Central region of the U.S.A. These soils had been used by Barber et al. (1961) in greenhouse studies in which they grew millet on unfertilized, undried samples and determined the yield of K in the millet. Most of the 20 soils selected were from the same series, but different samples, as the samples used in the release studies presented in Figure 11.

Ten-gram samples of air-dry soil were added to 7 ml. of water and 20 ml. of n-octanol in 50 ml. beakers. They were then heated for 60 hours on a steam hot-plate located in a fume hood. The beakers were covered with watch glasses for the first 12 hours of heating and uncovered for the remaining 48 hours. Exchangeable K was determined in these samples and in samples of the original untreated air-dry soil. As a second treatment to cause reversion, samples of the same soils were placed in 50 ml. beakers with 7 ml. of water and heated for 48 hours in an autoclave at 103° C. They were then

extracted with NH_4Ac and exchangeable K was determined. Data from these treatments are presented in Table 28 and Figure 19.

The aim of the octanol treatment was to lower the exchangeable K level of the air-dried soil to that of the undried soil. Examination of the data in Table 28 shows that for 9 of the ten soils whose exchangeable K value in the undried state was over 50 ppm., the values for the octanol treated samples were lower than the exchangeable K in the undried soil. Three of these soils fixed K on drying with no additions. For these soils it was not expected that octanol treatment would result in the same exchangeable K values as for the moist soils. For the remaining 6 soils with moist exchangeable K values over 50 ppm., however, octanol treatment resulted in reversion, and fixation, of K to the extent that exchangeable K values were below those of the moist soil. In soils with low exchangeable K levels in the undried state the octanol treatment resulted in some reversion of K, but not sufficient to reach the original moist exchangeable K level. This pattern is illustrated by the regression lines in Figure 19. Thus, the octanol treatment has resulted in some soils having more exchangeable K than the undried soils and some having less. It had been assumed that the exchangeable K value of the moist soil would be a rather definite point beyond which reversion of K would not readily occur. The data which have been presented suggest, on the contrary, that the exchangeable

Table 28. Exchangeable K values and yield of K in millet grown on unfertilized undried samples of 20 Midwestern soils

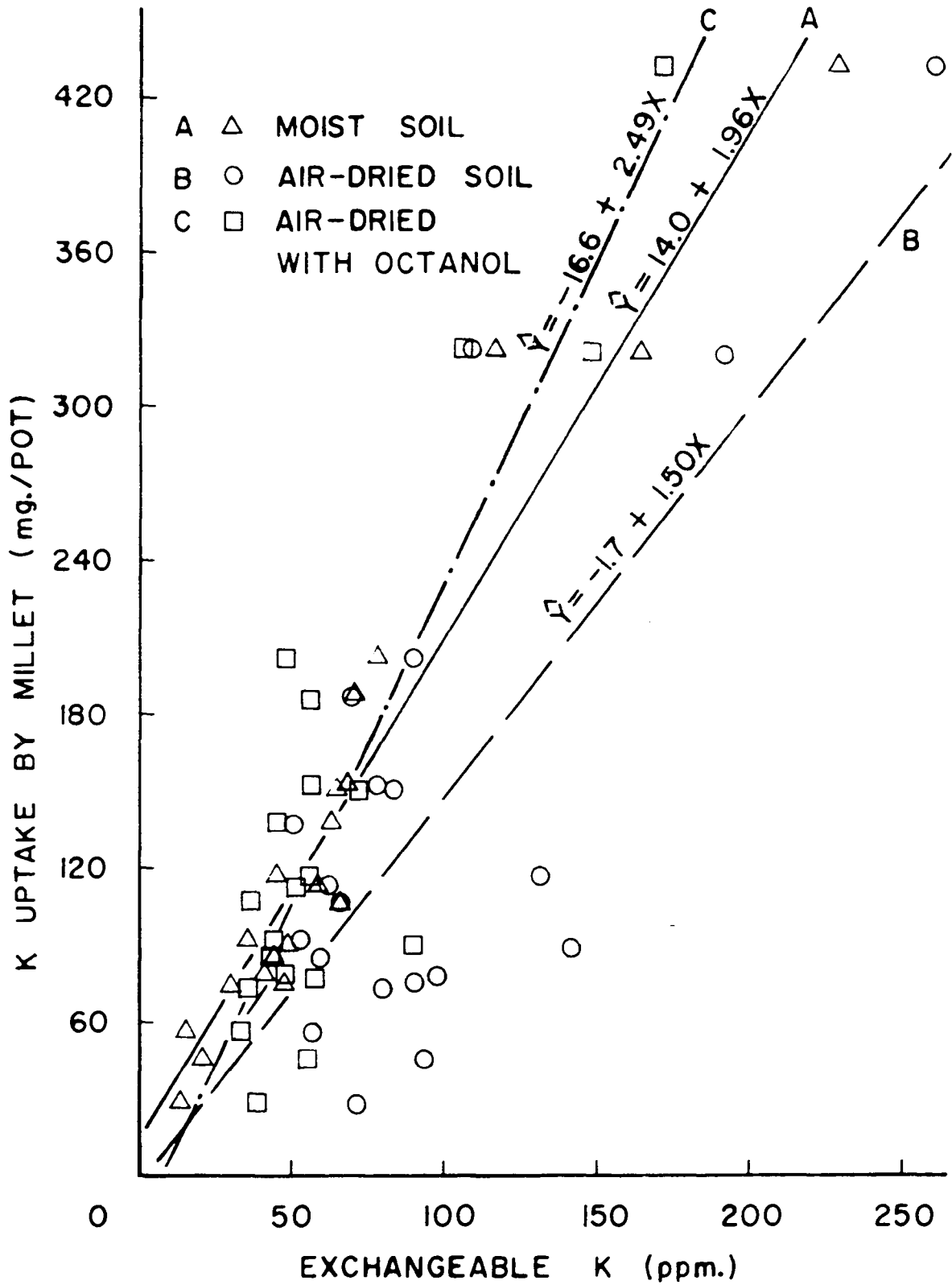
Soil	Depth in profile (inches)	Exchangeable K (ppm.)				Yield of ^a K in millet (mgm./pot)
		Un- dried ^a	Air- dried	Air- dried (octanol)	Air-dried re-wet	
Fox loam	18-24	58	62	52	69	113
Oshtemo sand	0-6	63	51	45	44	138
Metea sand loam	0-6	70	69	56	66	187
Hubbard loamy sand	0-6	116	108	106	112	323
Skyberg silt loam	18-24	30	80	36	65	74
Skyberg silt loam	18-24	14	72	39	67	29
Floyd silt loam	0-6	67	67	37	53	107
Carrington silt loam	0-6	65	84	72	84	151
Fayette silt loam	18-24	21	94	55	82	46

^aData obtained from Barber et al. (1961).

Table 28. (Continued)

Soil	Depth in profile (inches)	Exchangeable K (ppm.)				Yield of ^a K in millet (mgm./pot)
		Un- dried ^a	Air- dried	Air- dried (octanol)	Air-dried re-wet	
Carrington silt loam	0-6	43	60	43	56	85
Carrington silt loam	18-24	16	57	34	54	57
Fayette silt loam	0-6	78	90	48	72	203
Fincastle silt loam	18-24	48	91	58	88	77
Fincastle silt loam	18-24	45	132	56	114	117
Elston silt loam	0-6	67	78	56	73	152
Summit silt loam	0-6	164	192	148	173	321
Wabash silt loam	0-6	228	260	171	244	432
Cherokee silt loam	18-24	49	142	84	114	90
Cisne silt loam	0-6	36	53	44	53	92
Clyde loam	0-6	42	99	48	67	78

Figure 19. Potassium uptake by millet from undried soils plotted against exchangeable K extracted from undried, air-dried, and air-dried-octanol treated soils



K value of the moist soil has little significance as a target for reversion.

From data presented with the Marshall subsoil (Figure 15) moist heating of previously dried soils would not be expected to reduce the exchangeable K values to those of the moist soils. It was considered possible, however, that the exchangeable K values resulting from moist heating would correlate well with K uptake by plants. Correlation coefficients were calculated to show the relation of K uptake by millet with exchangeable K extracted from the moist soils, the air-dry soils, the air-dried octanol treated soils, and the air-dried soils heated moist in an autoclave. These correlation coefficients are presented in Table 29 along with coefficients

Table 29. Correlations between exchangeable K values in moist, air-dried, air-dried octanol treated and air-dried re-wet soils, and between these exchangeable K values and K uptake by millet from undried unfertilized soils

Soil sample	Coefficients of correlation for exchangeable K	
	With K uptake by millet	With exchangeable K in undried soil
Undried	0.96	
Air-dried	0.74	0.82
Air-dried, octanol treated	0.88	0.92
Air-dried, re-wet	0.79	0.86

showing the relation of exchangeable K extracted from the moist soil to the exchangeable K extracted from samples receiving the other three treatments.

The exchangeable K values from the air-dried soil showed

the lowest correlation with K uptake by millet while those from the moist soils showed the highest correlation. Moist heating of the soils produced exchangeable K values that correlated with K uptake only slightly better than the values from air-dry soils. The octanol treatment, however, resulted in an appreciable increase in the correlation of exchangeable K with K uptake by millet over that obtained with the air-dry soil. This treatment appears promising as a method of improving exchangeable K values as an index of plant available K. The exchangeable K values obtained do not correlate as well with K uptake as do exchangeable K values obtained from moist soils, but the problems associated with using moist samples are avoided.

SUMMARY AND CONCLUSIONS

The main objective of these studies was to search for factors which affect release of K on drying and to study these factors in an effort to understand the mechanism involved. A second objective was to find a method of drying soils without changing the exchangeable K values and to find a method of treating dried soils so that the exchangeable K extracted would be the same as from the undried soils.

Miscellaneous Soil Treatments

It has been shown by Hanway et al. (1961), among others, that many Midwestern soils release K on drying and that this K does not entirely revert to non-exchangeable form again on re-wetting. These changes have been shown to occur in the Marshall subsoil which was used for most of the studies reported in this manuscript.

It was shown that, along with the K released to the exchangeable form on drying, an equal amount of Ca appeared to be released and small amounts of Na. Exchangeable Mg appeared to decrease on drying, but the results were not consistent with degree of drying and the changes were small. Thus it was not possible to conclude from these data that cation exchange is responsible for the release of K that occurs when soils are dried.

It was shown that hot NH_4Ac extracted less K from dried

soil than cold NH_4Ac . Reversion of K in presence of water was also shown to be faster at higher temperatures. It was therefore suggested that some reversion may be occurring in presence of NH_4Ac and that the effect of temperature on reversion is responsible for the smaller amount of K extracted at higher soil and extractant temperatures.

At moisture levels below the air-dry state, rate of drying affects the amount of K released from the Marshall subsoil, slow drying resulting in more release. This would indicate that release of K is not an instantaneous result of water loss, but takes some time to occur. It is therefore suggested that a chemical reaction is involved.

Addition of water to soils before drying was shown by Scott et al., (1957) to reduce release of K. Similar results were obtained with the Marshall subsoil. Shaking of the soil and treatment with high frequency sound caused appreciable reductions in K release on drying. Thus, dispersion of the soil appears to reduce release and it is suggested that the reduction in release when water was added was due to dispersion by the water.

Addition of NaCl before drying reduced the amount of K released in the Marshall subsoil, supporting the findings of Scott et al. (1957) with Harpster and Fayette soils. Treatment with dithionite or with Dowex A-1 chelating resin to remove Fe and organic matter reduced the amount of K released on

drying. The Na added in these treatments and the dispersion involved were believed to explain the reduction in K release observed, however.

Samples of Marshall subsoil were extracted 11 times with 0.1 N NaCl, CaCl₂ and NH₄Cl followed by oven drying after each extraction. On the first extraction, before drying, NH₄ removed the most K, but on subsequent extractions, after drying, more K was extracted in presence of Ca than in presence of Na or NH₄. The amount of K removed per extraction decreased only slightly as the number of extractions increased and there was no indication that the total amount of release was approaching a limit. It was concluded that no characteristic, limited amount of K is susceptible to release in a particular soil. The release of K by drying is, however, characteristic of the cation on the exchange complex of the soil.

The Effect of Organic Additives on Potassium Release

It was reported by Scott and Hanway (1960) that additions of various solvents affected release of K on drying. A wide range of organic compounds were added to samples of moist Marshall subsoil followed by drying at 110° C. Many of the compounds tested reduced release of K on drying to some extent. Alcohols, sugars, ketones, and aldehydes were all effective to various degrees but CCl₄, benzene and ether had no effect. Examination of some physical properties of the effective

additives showed that under the conditions studied, dielectric constant, dipole moment and solubility in water were not closely related to their ability to prevent release of K. Boiling point and molecular weight, however, were related to the effect of compounds on K release.

According to Coulomb's law, the force acting between two charged particles is inversely proportional to the dielectric constant of the medium when the charge on the particles and the distance between them remains constant. Thus, the attraction between the K ion and the charged clay lattice would be affected by the dielectric constant of the medium. It was therefore expected that the dielectric constant of the additive would affect K release if ion exchange were involved. The fact that a relationship between dielectric constant and K release was not observed would suggest that K release is not an exchange phenomenon. Further studies with organic additives have shown, however, that the results obtained in this study of the dielectric effect were confounded by the method used. It has been found that even ethanol will completely prevent release of K if it is maintained on the soil while water is being lost. Although ethanol has a dielectric constant considerably higher than dioxane it is much less than that of water. It is possible therefore that dielectric constant does influence K release but that the organic compounds tested all have dielectric constants low enough to

completely prevent release.

Studies with normal alcohols showed that when applied before drying octanol and hexanol were more effective in preventing release of K than alcohols of shorter carbon chain length. Investigations with the four butyl alcohols, which all have the same molecular weight, demonstrated that the straight chain member was more effective. With normal alcohols the boiling point increases with chain length and with butyl alcohols the boiling point is higher where there is less branching. Thus, in both these cases the compounds with higher boiling points were more effective.

When the exchangeable K extracted from the Marshall soil after drying was plotted against milliliters of additive applied before drying, it was noted that the curves for the less volatile compounds, octanol, glycerol, sucrose and dextrose, were almost identical. When rates in moles of these same additives were plotted, the curves were quite separate. From this it is suggested that the effect of the additives in preventing release is probably physical. If their effect was chemical it would be expected that they would be similar in effect when plotted on a molar basis or on the basis of hydroxyl groups.

Addition of water to Marshall subsoil along with the more volatile alcohols reduced the effectiveness of these compounds in preventing release. Less volatile compounds were less

affected by water additions. Glycerol with a boiling point of 290° C. and dextrose which is not volatile at 110° C. prevented release as completely when added with large amounts of water as when added with small amounts. Most of the organic compounds were less effective in preventing release when dried rapidly in a forced-draft oven than when dried slowly in a gravity-draft oven. Once again, however, the effectiveness of higher boiling point compounds was less and dextrose was equally effective at both drying rates.

When volatile organic compounds are added to a moist soil and heated at 110° C., the water and organic compound evaporate. It appears probable that more volatile compounds evaporate before all the water is driven off and therefore do not prevent release simply because they do not remain on the soil until all the water has been lost. This would explain why water additions reduce the effectiveness of the more volatile compounds in preventing K release. It is suggested that more volatile compounds are less effective in preventing release in a forced-draft oven than in a gravity-draft oven because the more rapid drying in the forced-draft oven tends to minimize differences in evaporation rate between water and the organic compound.

If the ability of compounds to remain on the soil while water is lost controls their ability to prevent release, it seems probable that the strength with which the compounds are

adsorbed on the soil would be important. Certain compounds are not as effective in preventing release as their boiling point would suggest they should be. Cyclohexanol, for example, is not as effective in blocking release as hexanol although its boiling point is higher. It may be that these compounds are less strongly adsorbed on the clay.

If differences in the effectiveness of various alcohols in preventing release are due to differences in their persistence on the soil, it should be possible to prevent release with some of the more volatile compounds by maintaining them on the soil. Ethanol was one of the less effective compounds in reducing release even at very high rates of addition. It completely prevented release, however, when it was maintained on the soil by frequent additions while heated at 75° C. for 24 hours, and then heated another 24 hours without additions. Thus, it has been confirmed that the alcohols need only be maintained on the soil until the water has been driven off to block release of K.

Experiments were conducted to study the persistence of organic additives on the soil. It was shown that some of the compounds which were more effective in preventing release did persist after oven-drying, but even those which showed little persistence were capable of reducing release on K on drying quite considerably. Extraction of K from oven-dried soils in presence of some of the more persistent additives showed that

they did not interfere with extraction of K. It was therefore concluded that these compounds do actually prevent release of K on drying rather than simply preventing extraction of K which has been released.

Dextrose was shown to block release of K from the Marshall subsoil when added with different amounts of water or dried at different rates. Ten ml. aliquots of 2 M dextrose solution were therefore added to 10 g. samples of 20 Mid-western soils followed by drying at 110° C. for 48 hours. This treatment effectively prevented release of K from those soils which otherwise release K on drying. Thus, one of the objectives of these studies was achieved. This would suggest that the effects shown in the Marshall subsoil are generally applicable to other soils that release K on drying.

The Marshall subsoil was heated at 110° C. for various periods of time in a gravity-draft oven, where it was allowed to dry, and in an autoclave, where it was kept moist. Heating under drying conditions resulted in large amounts of K being released in the first few hours with the rate of release decreasing until approximately the tenth day when it appeared to have stopped. When the soil was heated without drying, K release amounted to approximately 35 ppm. at the end of 40 days compared to 235 ppm. at the end of 40 days when dried. Release during moist heating appeared to be continuing at the end of the 40 day period. When the soil was heated in the

oven after addition of cyclohexanol, the exchangeable K values were quite similar to those obtained with heating in the autoclave with no additions.

The K released when the soil was heated moist at 110° C. can be considered as that release due to temperature while that K released on heating in the oven at 110° C. is due to temperature and drying. It may be concluded that, of the large amount of K released on drying at 110° C., only a small portion is due to temperature alone and the remainder must be due to loss of water. The addition of cyclohexanol before drying appears to have blocked that release due to loss of water, but not the portion due to temperature. Exchangeable Na values were determined in the same experiment. Very small amounts of Na were released on heating dry in the oven, but more Na than K was released on moist heating in the autoclave.

Potassium Reversion

Reversion may be defined as the fixation of K which has been released by drying. The K released by soils on drying does not completely revert on re-wetting to produce the exchangeable K value in the original moist soil. Studies with the Marshall subsoil showed that on addition of moisture to the dry soil, reversion was quite rapid initially, but soon became quite slow. Air-dried soils reverted to lower exchangeable K values when re-wet than oven-dried soils and

reversion was faster at 90° C. than at room temperature. It was concluded from these studies that the degree of reversion attained on re-wetting a dried soil depends on the degree of drying and that the rate of reversion is affected by the temperature of moist incubation. Even with air-dry soil and the higher temperature, however, the exchangeable K value after reversion was still twice as large as that of the undried soil.

Organic additives caused some reversion of K when added alone and left at room temperature or heated. These effects are believed to be due to water contained in the organic chemicals. Organic additives had no effect on reversion when they were added with water and left at room temperature. Addition of organic compounds and water to the dried soil followed by re-drying, however, did produce considerable reversion of K. Although it was apparently necessary for the soil to be wetted with water for reversion to occur, large additions of water reduced the effectiveness of organic additives, as it did in release studies. Addition of the more volatile compounds was also less effective when the soil was dried in a forced-draft oven instead of a gravity-draft oven. The longer chain normal alcohols were more effective than those with shorter chains, as they were in release studies. To determine whether less effective compounds would result in reversion if maintained on the soil, cyclohexanol and ethanol

were added to oven-dry Marshall subsoil with water and replenished as required while water was lost by drying. Cyclohexanol resulted in complete reversion and ethanol nearly so, indicating that as with release, the compound only had to be maintained on the soil while water was being lost to be completely effective.

It is suggested that K release and fixation probably occur simultaneously when a soil is dried. When water and organic compounds are added to an oven-dry soil and the soil is re-dried, it is suggested that the organic compounds prevent release of K. At the same time the K, previously released, is fixed by collapse of the clay mineral lattice as water is driven off on re-drying. Thus, while the net result of adding the organic compound is an increase in reversion of K, it is suggested that the additive only prevents release, so that the reversion which occurs is more apparent. This explanation would account for the observation that water must be added to obtain reversion with organic additives, and that drying was required. It also explains the similarity in the ability of additives to block release and cause reversion. Scott et al. (1957) showed curves for exchangeable K values plotted against water content for three Iowa soils. At certain levels of added K the curves show that the exchangeable K decreases with moisture loss at high moisture levels, but increases with moisture loss at low moisture levels. These

results also support the above suggestion that release and fixation can occur independently, in the same soil sample.

Glycerol and sucrose additions were not effective in causing K reversion whereas octanol additions were quite effective. In release studies, on the other hand, these additives behaved like octanol in that they were more effective in preventing K release than any other compounds tested. Neither glycerol nor sucrose is lost on heating and it was concluded that their presence on the clay mineral lattice prevents its collapse and hence prevents fixation of K. Thus, reversion was limited to that occurring on heating moist, even when the sample was dried. When sucrose and octanol together were added, along with water, to the oven-dried Marshall subsoil followed by re-drying, the resulting exchangeable K values were nearly as high as where sucrose was added alone and considerably higher than those where octanol was added alone. This would support the conclusion that sucrose actually blocks reversion of K by its presence.

Addition of 20 ml. of octanol to 10 g. of soil followed by heating for 60 hours on a steam hot-plate was found to be a simple but effective method of obtaining complete reversion in the Marshall subsoil. This treatment was applied to 20 air-dry Midwestern soils in an effort to obtain the same exchangeable K values as in the moist soils. The treatment with octanol resulted in more than sufficient reversion to

obtain the moist exchangeable K values in some soils, and less than required in others. In general, for soils whose moist exchangeable K values were greater than 50 ppm., the octanol treatment resulted in exchangeable K values below those of the undried soil. For soils with moist exchangeable K values below 50 ppm., the octanol treatment, in most cases, resulted in exchangeable K values higher than those of the moist soil. It had been assumed that the exchangeable K value of the moist soil would be a rather definite point beyond which reversion of K would not readily occur. The data presented suggest, on the contrary, that the exchangeable K value of the moist soil has little significance as a target for reversion, at least with the octanol treatment.

Correlation coefficients were calculated for the relation of K uptake by millet, grown on undried, unfertilized soils, to exchangeable K in the moist, air-dry and air-dried octanol treated samples. These data show that the exchangeable K values of the octanol treated samples do not correlate with K uptake as well as those for the moist soil, but do correlate with K uptake considerably better than the exchangeable K values for the air-dried soil. The octanol treatment is simple to apply and avoids the problems involved in using moist samples for routine exchangeable K determinations. For these reasons it appears promising as a means of obtaining more meaningful K determinations from air-dried soils than the

exchangeable K values currently used in soil testing laboratories.

Regarding the Mechanism of K Release

Alexsandrov (1950) has stated that release of K on drying and fixation on re-wetting were bacterial and considerable evidence against such a mechanism was presented earlier in this manuscript. One experiment presented in these studies appears to offer rather conclusive evidence on such a mechanism. Alexsandrov suggests that when soil is dried the bacteria are killed, releasing K and that on re-wetting the bacterial population increases again and fixes K by assimilation. The data presented in Figure 15 show that when an oven-dry soil is re-wet and incubated at 90° C., K reverts, or is fixed, quite rapidly. It would appear that reversion at this temperature could not be due to increased bacterial populations and that the mechanism suggested by Alexsandrov cannot be the cause of release and reversion on drying and re-wetting.

Scott et al. (1957) showed evidence for and against release being an exchange phenomenon. Some of the data presented in this manuscript support the concept that K release is an exchange reaction. The fact that the amount of K released is a function of the ion saturating the exchange complex (Figure 3) would suggest that release is some sort of

exchange reaction. It was shown also that release was greater with slow rates of drying. This would suggest a chemical reaction, possibly exchange.

Some of the data presented are more difficult to explain on the basis of ion exchange. The exchangeable K, Na and Ca all increase on drying while Mg decreases only slightly, if at all. An exchange phenomenon would not appear to explain release of Ca and Na as well as K. The reduction in K release brought about by dispersion of the soil is not readily explained by exchange. Neither is the effect of organic compounds in blocking release easy to explain on the basis of exchange. Dielectric constants of the organic compounds did not appear to be related to differences in effectiveness in blocking release, as would be expected if their effect concerned an exchange reaction. There is a possibility, however, that dielectric constant was not studied in the range where it is important. The fact that octanol, glycerol, sucrose and dextrose appear to be equally effective on a volume basis, but not on a molar basis suggests that the effect of these compounds on K release may be physical rather than chemical.

At the present stage of knowledge no conclusions appear justified as to the mechanism of K release on drying. It appears that more knowledge about release is needed before the mechanism may be determined. The use of organic additives to control K release, however, should help solve some of the

practical problems involved in obtaining meaningful exchangeable K values from dried soils and should provide a useful tool for use in studying release, reversion and fixation of K.

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