DETERMINATION OF THE ADSORPTION AND MOVEMENT
OF 2,3,6-TRICHLOROBENZOIC ACID IN SOIL
AS INFLUENCED BY SOIL TYPE AND WATER PERCOLATION

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INTRODUCTION

The direct application of herbicides to soils for weed control has become a practice of major importance in crop production. This offers certain advantages compared with the foliage application of herbicides. Soil treatments are used selectively between weeds and crops and also as soil sterilants.

In many cases, one application will give control of the weeds for an entire crop season. Other chemicals not selective on crops have been used to kill patches of deep rooted perennial weeds. TBA is a chemical which has shown considerable promise for the control of deep rooted perennial weeds. This material is absorbed by foliage and translocated to the roots of plants. It is also absorbed by the roots, which makes it a soil active herbicide.

Visualizing the soil as a living complex or medium, it is important to investigate the action and behavior of herbicides in soil.

Of primary importance to the utility of a compound as a soil active herbicide is the rate of disappearance, a phenomenon involving a complexity of factors. Breakdown of the herbicide by micro-organisms, adsorption by

the soil particles and leaching are important phenomena which affect the residual life of a chemical in the soil.

The purpose of this thesis is to study two of these factors, namely adsorption and leaching, as they influence the movement of 2,3,6-trichlorobenzoic acid (TBA) in three soil types. To carry out this study, it was necessary to determine some of the chemical properties of TBA, and find methods for extraction and identification of this compound.

REVIEW OF LITERATURE

Properties of Benzoic Acids

According to Koepfil, Thiman and Went (12, p. 779) a compound, in order to be active as a growth regulator, must meet the following minimum requirements in molecular configuration:

A.   A ring system nucleus

B.   A double bond in the ring

C.   A side chain

D.   A carboxyl group on the side chain

E.   A particular space relationship between the ring and the carboxyl group.

The chloro substituted derivatives of benzoic acid do not fully meet these requirements since the carboxyl group is not one carbon atom removed from the ring.

Zimmerman and Hitchcock in 1942 (34, p. 321-343) working with 2-bromo 3-nitro benzoic acid, and 2-chloro 5-nitrobenzoic acid, found these two compounds were active when a bromine and nitrogen group was substituted in the proper position in the ring.

Bentley in 1950 (1, p. 449) confirmed the growth regulating activity of chlorobenzoic acid. Both 2,3,6-trichlorobenzaldehyde and 2,3,6-trichlorobenzoic acid

were active in the Avena coleoptile test. In this test
2,3,6-trichlorobenzaldehyde was more active than β indole-
acetic acid. Bentley found 2,3,6-trichlorobenzoic acid
was less active at higher concentrations, but more active
at low concentration compared to the aldehyde.

Zimmerman and Hitchcock (35, p. 213) found 2,3,6-tri-
chlorobenzoic acid and 2,3,6-trichlorobenzaldehyde caused
cell elongation, proliferation of tissue, induced adven-
titious roots, modified the pattern of leaves and other
organs, and caused parthenocarpic development of fruits.

The same investigators in 1952 (36, p. 427) obtained
similar results with 2,3-dichlorobenzaldehyde, 2,6-di-
chlorobenzoic acid, and 2,6-dichloro-3-nitrobenzoic
acid. The aldehyde of 2,6-dichlorobenzoic acid was some-
what less active. It caused formative effects, but did
not cause cell elongation, cell division and adventitious
roots as did the acid.

Muir and Hansh (20, p. 369-374) studied the cell
elongation effects of a wide variety of substituted
benzoic acids, to compare the relationships of structure
and plant growth activity of these compounds. Substituted
benzoic acids, with an electronegative atom or group
capable of displacement by an electron-rich substrate in
one or both ortho position, was found to promote cell

elongation of Avena coleoptile sections.

Tetrachloro and pentachloro benzoic acids also show
inhibitory responses, according to work conducted by
Miller (17, p. 187). The compounds 2-ethyl hexyl-2,3,4,5-
tetrachloro benzoate, 2,3,4,5-tetrachlorobenzoic acid and
pentachlorobenzoic acid, inhibited the growth of bean
plants at less than 0.23 percent. Pre-emergence weed
control was obtained in greenhouse tests with penta
chlorobenzoic acid at 5 pounds per acre with no injury
to corn.

Jones et al. (11, p. 422-454) showed the selectivity
of 2,3,6-trichlorobenzoic acid and aldehyde were similar
to that of 2,4-D type compounds.

Many research workers have conducted tests to
evaluate the chlorobenzoic acids as herbicides. Chilcote
and Furtick (3, p. 49) in a test comparing substituted
urea herbicide, dinitro amine, 2,4-D amine, and trichloro-
benzoic acid for weed control in corn, reported one, two,
and three pound rates of trichlorobenzoic acid were more
effective than 2,4-D amine or dinitro amine for pre-
emergence weed control.

Interest in these compounds was increased when they
were tested as soil applications in pre-emergence treat-
ments. According to Furtick (7, p. 33-39) they showed
high effectiveness against the germinating seedling of a

large number of weed and crop plants.

Major interest in these compounds shifted to perennial weed control when the compounds were found to kill perennial morning glory (Convolvulus arvensis). Morning glory studies by Swan (27, p. 6, 28 p. 11) created real interest since morning glory is one of the major perennial weed pests in many countries of the world.

Swan reports three pounds per acre of TBA controlled 49 percent of morning glory, compared with 20 percent control with three pounds of 2,4-D amine. Heavier rates, 40 pounds per acre, of TBA, controlled 99 percent of this weed compared to 95 percent for 80 pounds per acre of 2,4-D amine. When rows of fall wheat were seeded in the plots to determine injury, from the residual chemical, no reduction was observed in the stand or vigor of the wheat.

Minnarik (18, p. 4) evaluated 2,3,6-trichlorobenzoic acid as a temporary soil sterilant for the control of perennial weeds. Rates of 4 to 5 pounds per acre controlled field bindweed (Convolvulus arvensis), Russian knapweed (Centaurea repense), leafy spurge (Euphorbia esula), cattails (Typha latifolia), and halogeton (Halogeton glomerata). Quackgrass (Agropyron repens), another important weed, showed high sensitivity to this compound; the 2 to 4 pound rates per acre gave 40 to 70 percent control of this weed with no injury to corn.

Leavitt (14, p. 29) reported this herbicide has also been evaluated for the control of woody vines and brush, such as salmonberry and certain wild blackberries.

Furtick (7, p. 39), in a review of the polychlorinated benzoic acids, indicated injury symptoms could be detected on sensitive plants a year after the use of chlorobenzoic acids as pre-emergence herbicides.

The residual life of this compound in the soil appears to be strongly influenced by the amount of rainfall and soil type. Swan (28, p. 11) reported some cases where rows of fall wheat seeded in plots sprayed with TBA were not injured, but with less rainfall injury was detected.

Adsorption and Herbicide Action

Robbins, et al. (23, p. 243) pointed out the inherent toxicity of chemicals are reduced by leaching and decomposition of the chemical. Adsorption of the chemical by the soil is a factor which determines the herbicidal effects of soil sterilants.

Hill (10, p. 43) indicates that whether a herbicide is used pre-emergence or as a soil sterilant, the effectiveness is dependent on movement, activity and residual period in the soil. The activity or efficiency of a herbicide in the soil is dependent on the amount of the chemical in the woil solution in the root zone. The amount of herbicide in

solution is dependent or influenced by the adsorption capacity of the soil and the solubility of the compound.

In some cases, depending on soil type, the chemicals may be adsorbed on the soil particles and become unable to exert herbicidal action. In other cases, herbicides, even though adsorbed on the soil particles, may be in an available form to plants and this adsorption only contributes to the retention of the chemicals in the upper layer of the soil.

Adsorption has been defined by Kittsley (12, p. 81) as the concentration of a substance at a surface, as distinguished from absorption, in which the molecules penetrate among the molecules of the absorbent.

Prutton and Maron (22, p. 226) explain this concentration of molecules at a surface. Molecular forces at the surface of a liquid are in a state of unbalance or unsaturation. The same is true for the surface of a solid. Solid and liquid surfaces tend to satisfy these residual forces by attracting and retaining on their surfaces gases or dissolved substances with which they come in contact. Adsorption from solution follows the same general principles as for the adsorption of gases. With both, an increase in temperature operates to decrease the amount of adsorption. An increase in the surface area

of the adsorbent results in an increased adsorption. Adsorption of solutes, like that of gases, involves the establishment of an equilibrium between the amount adsorbed on the surface and the concentration of the substance in solution.

Dean (5, p. 67) pointed out that even though adsorption for solutes follows laws very similar to those which govern adsorption for gases and vapors, there is one difference which makes the former rather complicated. Solutions always involve displacement so there is both adsorption and desorption which reaches an equilibrium.

Two types of adsorption can be distinguished. Physical adsorption, known as van der Waals adsorption, is characterized by low heat of adsorption. All gases exhibit van der Waals adsorption. In some cases Kittsley (12, p. 83) and Glasston (8, p. 1201) the second type of adsorption, called Chemisorption, which involves forces of a chemical nature, may ensue, especially at high temperatures.

Some materials are more strongly adsorbed than others Dean (5, p. 67). Chemical similarities between the sorbent and the sorbate, are believed to be one explanation of this preference of sorbents for certain materials. Charcoal, which is a porous carbon, has a graphite structure

resembling the aromatic hydrocarbons and adsorbs benzene
and other organic vapors much more strongly than water.

Williams (32, p. 92-93) offers another explanation.
In relation to the use of chromatography, some compounds
have structural affinity for others. Olefinic linkage
in the molecule has a definite relationship to adsorption
affinity. The series $C6H6-(CH=CH)n-C6H5$ has been shown
to decrease in affinity as n decreases. Similar results
have been reported for many of the polycyclic aromatic
hydrocarbons. If two such compounds are formulated with
the same number of double bonds, then the one with the
least number of rings is found to be most strongly ad-
sorbed.

The most common and practical method of recording
adsorption data is in the form of adsorption isotherms,
in which the specific amount of the substance adsorbed
is plotted against the equilibrium concentration of the
substance. These data are taken at definite temperatures,
which give the curve the name isotherm.

According to Dean (5, p. 76-78), the theory of the
Langmuir isotherm is based on the following assumptions:

1. A molecule of a gas which strikes a surface will
   stick and evaporate after spending an average
   time on the surface.

2. The rate of evaporation from the surface is proportional to the fraction of the surface which is covered. This is another way of saying that each molecule evaporates independently.

3. A molecule of gas which strikes an adsorbed gas molecule will be reflected.

The Langmuir adsorption isotherm can be expressed as:

$$x/m = ab/(1+aP)$$

$$P/(x/m) = 1/ab = P/b$$

The (a) term in the Langmuir equation is a multiplier of the pressure. A large value of (a) means that sorption will approach completion at low pressure and the isotherm will have a sharp curve. The (b) term multiplies the whole expression and at a high pressure x/m will be proportional to b. An adsorbent which follows an isotherm with a large (b) term will have a large capacity.

An important application of adsorption from solution is to be found in the method of chromatographic analysis, the principle of which was first used by the Russian scientist, M. Tswet (1926), but not widely applied until R. Kahn (1931) employed it in connection with work on carotenes.

The procedure is based on the fact that a given solid may adsorb to a varying extent different constituent of a mixture present in solution. If such a solution is poured down a long column packed with the powdered adsorbing solid, the material taken up by the upper layer will consist largely of the solute that is most readily adsorbed, together with lesser amounts of the others.

Chromatographic analysis can be divided into adsorption chromatography, partition chromatography, and ion exchange chromatography. According to Zechmeister (33, p. 20-22), ion exchange involves the release of some constituent from the solid surface to the liquid phase, in which those ions for which the exchange affinity is strongest are retained near the top, while others penetrate lower sections of the column.

Since the development of synthetic resins as ion exchangers, great interest has been shown by scientists in the field of chromatography. The ion exchangers are all polymeric or macro molecular substances. They are insoluble in ordinarily used solutions like water, and thus serve to immobilize the ions which they bind.

Cassidy (2, p. 267) has classified the ion exchangers into inorganic and organic. Each classification can be

subdivided into anion and cation exchangers, but under some conditions synthetic resins are capable of either anion or cation exchange.

The mechanism of the ion exchange resins is based on the same mechanism by which cation exchange occurs in the soil. This involves the adsorption forces of the soil colloids. Ions adsorbed or fixed on colloidal particles may be replaced by ions having charges of similar sign.

Lyon et al. (16, p. 97-99) explained this phenomenon by means of a simple formula. When a mineral soil, high in replaceable calcium, functions under optimum conditions with considerable CO_2, which involves the presence of carbonic acid in the soil solution, the H-ions thus generated are exceedingly active and will tend to replace the exchangeable calcium of the colloidal complex.

This is based on the supposition that if calcium ions are easily displaced by H-ions, the latter are more strongly adsorbed than calcium ions, according to the following reaction:

$$Ca^{++}\boxed{Micelle} + 2H^- \xrightleftharpoons[H]{H} \boxed{Micelle} + Ca^{++}$$
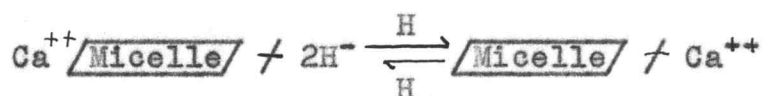
The direction of this equation depends mainly on the concentration of the different ions which can act in response to mass action. The soil is thus in a dynamic

state in which this reaction can go in either direction according to the amount of replaceable ions.

The cation exchange capacity of different soils is expressed in milliequivalent. This term is defined as one milligram of hydrogen or the amount of any other ion that will combine with or displace it.

The resistance of herbicides to downward movement in the soil may be governed by their adsorption on the soil constituents. Adsorption modifies activity of herbicides and also influences leaching.

In considering the effect on activity, Weaver (31, p. 84) studied the degree of adsorption of several growth regulators by certain ion exchange materials. The growth of plants in soil containing ion exchangers upon which NH_4 2,4-D was adsorbed, showed the adsorbed growth regulator was non-toxic. Barley and white mustard plants grew well in gravel-Zeo-Kash H mixtures containing NH_4 2,4-D at concentration of 10 and 100 mg respectively per pound of mixture.

Sherburne and Freed (24, p. 937), in a study of the rate of adsorption of 3(p.chlorophenyl)1,1dimethylurea on different soil types, reported a statistically significant correlation between adsorption and the amount of clay in the soil. The conclusion was that CMU in soils high in organic matter was somewhat less effective. This loss of

chemical activity was a result of strong adsorption; therefore, higher dosages were recommended for such soil.

Sund (26, p. 58) reported a strong correlation between amino triazole disappearance and base exchange capacity. When the order of least amino triazole disappearance was ranked for each soil type, it was found to be almost in direct proportion to the magnitude of the respective base exchange and clay content.

Sherburne and Freed (24, p. 937), in a study of adsorption of CMU by different soils, found the herbicide established an equilibrium between the adsorbed phase and the solution. In another study with the same compound, Freed (6, p. 19-25) found the reason CMU had a different behavior in different soil types was due to extreme differences in the bond energy of adsorption for this chemical on different soils. The determination of this bond energy of adsorption for various chemicals and soils was considered important and it may provide a basic understanding of the behavior of chemicals in the soil as influenced by leaching.

Leaching and Herbicide Action

Leaching is one of the key factors in determining the residual life of a herbicide in the soil. Adsorption influences the leaching. Strong adsorption of chemicals by the soil impedes removal by leaching. Low or lack of adsorption permits leaching to occur easily, dependent only on the solubility of the chemical.

There are some factors which can affect the amount of leaching. Amount, intensity, and frequency of rainfall are considered important. Organic matter, soil type, and soil moisture also influence leaching.

Upchurch and Pierce (29, p. 329), in a study of the influence of amount, intensity, and frequency of rainfall on leaching of monuron from Lakeland sandy soil, stated leaching involves two steps; the entrance of the herbicide into solution and the adsorption of the herbicide from the percolating solution by the soil. The intensity factor, apparently affects the latter step, but has little or no effect upon the former. Intensities of rainfall, when varied from 1/16 inches per application to 4 inches per application, had little influence upon the amount of monuron recovered from the 0 to 2 inch soil horizon. The conclusion was that more frequent rainfall resulted in a greater removal of monuron from the upper soil horizon.

Sherburne et al. (25, p. 53-54) studied the influence of soil type, precipitation and soil moisture on leaching of CMU. Leaching of this compound increased with greater water percolation, and was related to soil type. Leaching was greater in sandy soil than clay loam soil. The thermodynamic properties of the adsorbed CMU-water system was such that when the water passed through the soil, there was an alternate adsorption-desorption process occurring.

In a percolation study, comparing the leaching behavior of four herbicides (TCA, CIPC, NPA, and 2,4-D) in three soil types, Ogle and Warren (21, p. 271) found an interaction of herbicides and soil type in relation to herbicidal movement and retention. TCA moved rapidly in all soil types; 2,4-D leached readily in mineral soil, but was resistant to movement in muck soil; NPA moved readily in sandy soil, but was somewhat resistant to movement in the silt loam, and more resistant in muck. CMU was especially resistant to movement in muck soil. CIPC was highly resistant to movement in all three soil types.

In relation to soil moisture, Upchurch and Pierce (30, p. 29), in a study to find out the effect of soil temperature, organic matter, and soil moisture, on leaching of monuron, found that soil moisture content apparently

had little or no influence on leaching of this chemical.

Points used to explain these results were that the
rate of movement of percolating solution would be slower
in the wet treatment compared with the dry treatment, re-
sulting in greater retention of the herbicide by the upper
soil layer in the case of the wet soil. The percolating
solution which filled the soil interstices contained
herbicide in solution in the case of the dry soil treat-
ment and probably caused a greater retention of the chemi-
cal in the upper soil layers with the dry treatments. The
interstices in the wet treatment would already be filled
by moisture containing no herbicide and the percolating
solution containing herbicide would be excluded to a
degree, from the adsorption sites of the interstices.
Pre-wet soil, however, probably has a greater retention
capacity for organic molecules, compared with air dry
soil, and this relationship would cause the wet treatment
to retain more herbicide in the upper soil layers than
would the dry treatment.

Soil organic matter as a factor affecting leaching
of monuron, was found to be important. As the average
organic matter in the 0 to 8 inch layer of soil increased
from 0.87 to 1.44 percent, the amount of monuron retained
increased from 35 to 95 percent.

Hernandez and Warren (9, p. 292) found the same relationship of organic matter content of the soil to leaching. With 2,4-D application to soil low in organic matter, leaching was greater than for soils high in organic matter.

The review of literature leads to these general conclusions:

Adsorption is an important factor which exerts a strong influence on the behavior of herbicides when they are applied to the soil. Compounds are adsorbed by the soil particle to different degrees depending on their chemical affinity for the soil components. Soil type is a factor that influences the adsorption of chemicals. Apparently an increase in clay content or organic matter causes an increase in the degree of adsorption.

The leaching process is another factor which affects the activity of herbicides in the soil. This process is primarily influenced by soil type and adsorption. An increase in organic matter decreases the amount of leaching. Soil moisture and the amount, intensity, and frequency of rainfall are also important. Frequency and amount of rainfall becomes rather important in the removal of chemicals from the soil. Soil moisture and intensity of rainfall apparently have little influence on the leaching process.

MATERIALS AND METHODS

A. Materials

The soils used in this study were a sandy soil, Chehalis silt loam soil, and a peat soil, all obtained from western Oregon. The composition and properties of these soils are given in Table 1.

The trichlorobenzoic acid used in this study was 2,3,6-trichlorobenzoic acid, herein after referred to as TBA. One sample of TBA used in this study was obtained from the Hooker Electro Chemical Company. This was a purified sample containing 99+% of the 2,3,6-isomer. This sample was used as the standard for construction of the absorption spectra of TBA and the standard curve. Another sample of TBA used was obtained from Heyden Chemical Company. The Heyden sample was analyzed for the percentage of TBA by the ultra-violet method and gave a reading at 280 millimicrons, which corresponded nearly to that of the purified TBA.

B. Methods

1. Determination of the Properties of TBA

The chemical and physical properties of TBA were determined utilizing the standard procedures of organic chemistry (Morton 19, p. 1-261) and

(Daniels et al. 4, p. 1-568). Determinations were
made for solubility in various solvents, absorption
spectra, p^H of TBA solution and melting points.

The properties determined were felt to have an
important bearing on the behavior of TBA in the soil,
and would therefore be necessary to interpret the
results.

The solubility was determined by the equilibrium
saturation method. After saturation had been achieved,
an aliquot was withdrawn and the amount of TBA in
solution determined by ultra-violet absorption at 280
millimicrons and the reading compared to a standard
curve.

The light absorption spectra of TBA was determined
for the chemical in water, chloroform, and cyclohexane.
Readings were made starting at 270 millimicrons for
chloroform, 245 millimicrons for water, and 240 milli-
microns for cyclohexane.

In the preparation of a standard curve, a known
amount of the pure TBA was weighed on an analytical
balance and made to volume. Aliquots of this solu-
tion were withdrawn and diluted to a volume appro-
priate to give the desired concentration. Readings
were taken at the maximum absorption and a plot of

absorbency versus concentration was made to construct the standard curve.

2. Extraction of TBA from Water Solution and Soils

The technique used in determining the amount of TBA adsorbed by various soils required that a solution of the chemical be equilibrated with a known weight of soil. The supernatant solution, after reaching equilibrium with the soil, was then filtered off and the amount of TBA remaining in solution determined. In order to make this determination without interferences by soluble substances in the soil, it was necessary to extract the TBA from the supernatant liquid. Accordingly, a study was made of the solvents and methods required to achieve the best possible extraction. Standard solutions of TBA were shaken with twice the volume of solvent in a separatory funnel. After separation the organic phase was read on the DU spectrophotometer to determine the concentration of TBA in solution. This reading compared with the known original concentration of the water solution, made it possible to calculate the percentage recovery. Both chloroform and cyclohexane were used as extractants.

With volume of extractant held constant, single, double, triple, and quadruple extractions were investigated for efficiency of recovery. In addition, studies were made to compare various lengths of time for mechanical shaking.

Since TBA is a strong acid, it appeared desirable to investigate the influence of p^H on efficiency of extraction. A study was made of the recovery of TBA from water solution after acidification with hydrochloric acid. The technique consisted of a 2-minute shaking by hand using multiple aliquots of solvent with multiple extractions.

Extraction from Soil Solution

Investigations on the efficiency of TBA recovery by extraction of the supernatant liquid from the soil were carried out. As a strong acid, TBA could react with several of the cations present in a soil solution. Extraction from this supernatant liquid without acidification would indicate greater adsorption than actually occurred. Accordingly, adsorption after extraction for a non-acidified compared with an acidified soil solution was calculated. In order to obtain a clear solution, it was found necessary

to centrifuge after the initial filtration of the solution from the soil. The soil solution was then extracted directly or acidified with hydrochloric acid and extracted.

Extraction from Soil

Extraction of the chemical from the soil was made with a 6-place fat extractor. Extractions were carried out for a period of 6 to 14 hours with either chloroform or cyclohexane as the extractor. Comparisons were made of extraction efficiency between the two solvents. The cyclohexane proved to be the best solvent. In these extractions, aliquots of dry soil were placed in a thimble and extracted exhaustively with 50 milliliters of solvent. Upon completion of the extraction, the solvent was transferred to a volumetric flask, made to volume, mixed thoroughly, and an aliquot withdrawn for reading on the spectrophotometer.

Comparisons were made between extractions of soil acidified with sulfuric acid and non-acidified.

C. Study of the Adsorption of TBA by Different Soils

The amount of TBA adsorbed by three different soils was investigated by the equilibrium method. Forty gram samples of a sandy soil and Chehalis silt loam were used to determine adsorption. Eight grams of a peat soil were used. The three soil samples were mixed with 100 milliliters of three concentrations of TBA solution. The three concentrations of TBA were 76 ppm., 760 ppm., and 3,800 ppm.

Triplicate samples of the soil, plus the 100 milliliters of solution, were allowed to reach equilibrium for 12 to 14 hours at 20 to 21° C. At the end of the equilibrium period, the supernatant solution was filtered off, and centrifuged to clarify. Following centrifuging, 25 milliliters of the supernatant solution was removed, acidified with hydrochloric acid, and extracted with 4 aliquots of chloroform, consisting of 20-10-10-10 milliliters. The chloroform solution was placed in 50 milliliter volumetric flask, and after final extraction, made to a volume of 50 milliliters. An aliquot of this was then read at 280 milimicrons on the DU spectrophotometer.

Since the soil used was dry upon introduction into the equilibration flask, it was found necessary to correct the final concentration of chemical for the amount of water

adsorbed by the soil. Duplicate samples of soil were equilibrated against an excess of water, the water filtered off, and the amount of bound or adsorbed water determined by weighing. The concentration found in the supernatant liquid was then corrected for the amount of water lost by binding to the soil, and the true concentration calculated. It was then possible to calculate the number of micrograms of chemical bound by the sample of soil after dividing by the original sample weight, the micrograms of chemical adsorbed per gram of soil was calculated. The following is a sample calculation:

1. Calculation of water absorbed by soil

$$\frac{(\% \; H20 \; x \; gr \; of \; soil)-100}{\% \; of \; recovery} = \% \; of \; H20 \; abs.$$

2. $\dfrac{ppm \; recovered \; x \; \% \; H20 \; abs}{Sample \; Weight} = \gamma/gr$ of soil in final solution

3. γ/gr of soil original sol'n - γ/gr of soil in final sol'n = γ ads/gr of soil

A similar study was carried out with 2,4-D in Chehalis soil in order to compare the degree of adsorption between TBA and 2,4-D.

D. Leaching of TBA

For a study of the leaching of TBA in soils as a function of soil type, soil moisture, and cycles of moisture application soft glass test tubes .64 centimeters in

diameter and 16 inches long were drawn to a capillary on one end. In the capillary end of the tube, a plug of glass was inserted to prevent the soil from being washed on through the tube. Approximately 100 grams of mineral soil were packed uniformly into the tube to give a soil column of 12 inches. Aliquots of soil were introduced into the tube and packed by tapping the tube on the desk top after protecting it from breakage by inserting the tapered end into a cork or rubber stopper. This required about 100 grams of mineral soil and approximately 40 grams of peat soil, to give a uniformly packed column 12 inches long. Paper disks of filter paper, cut to the inside diameter of the tube, were then placed on these soil surfaces.

Aliquots, to give a heavy, medium, and light rate of application of TBA, were taken from a 3800 ppm. water solution of the chemical. The column was then leached with a predetermined amount of water. In certain instances the soil was air dry at the beginning of the leaching, and in other instances, it had been moistened to field capacity. The volume of water was calculated to determine the number of inches of rainfall represented.

Twelve hours after the last of the water had been introduced in the tube, the soil column was broken into

3-inch sections by filing the tube and breaking it. Each
section was then put into a beaker and 2 ml. of a 1 N
sulfuric acid solution added to obtain a p^H of 2. In the
case of the peat soil, this required 4 ml. of 1 N sulfuric
acid. The lowering of p^H by the introduction of acid, was
found to be necessary for the greatest efficiency in the
subsequent extraction of the TBA. After the soil had
dried, aliquots were introduced into the extraction
thimbles, and the soils extracted with cyclohexane. It
was found there was a volatilization of TBA during the
drying period. In order to determine the percentage re-
covery, two samples of soil containing 80 ppm. were
carried along to serve as a correction factor for per-
centage recovery. In addition, columns having no chemi-
cal added were also leached with water and handled in the
same manner as the treated columns, in order to correct
for the background adsorption of the soil.

After determining the concentration of TBA in the
cyclohexane, this was corrected to the true value by
multiplying by the recovery factor and subtracting the
appropriate soil blank. It was possible to calculate
from this the number of micrograms recovered in each
section of the column. From the total number of micro-
grams recovered from the column, the percentage in each

section was calculated to give an idea of the distribution pattern.

Comparisons in the leaching study included leaching as a function of soil type as determined in duplicate, starting with air dry soil. Another set of columns were compared for the leaching in different soil types, when they had been brought to field capacity before the chemical was applied to the column, and then leached with 3 inches of water. Finally a comparison was made of the rate of leaching in the Chehalis soil type, starting with air dry soil and adding the same amount of water in three different watering cycles. It was found that duplicates agreed very closely in their behavior.

In the final study, Chehalis soil was introduced into the column and 6 inches of water passed through the column in the following cycles: 6 inches, all introduced within 12 hours; 2 inches per day until the complete 6 inches were introduced; and for the third group, 1 inch per day until the entire 6 inches of moisture were introduced. After 12 hours for equilibrium the columns were broken up, and the chemical extracted, and the concentration in each section determined.

The data for the leaching studies were calculated in the following manner:

1. Calculation of factor of recovery

$$\frac{100}{(\% \text{ of recovery} - \% \text{ of volatilization})} = K$$

2. $K(x \text{ ppm recovered per section}) - \text{blank} = Y$

3. $Y(\text{am't of solvent used in extraction}) = \gamma \text{ recovered/section}$

4. $\dfrac{\gamma \text{ Recovered/section}}{\gamma \text{ Applied to column}} = \% \text{ of total recovered/section}$

EXPERIMENTAL RESULTS

The composition and properties of soil used in this study are given in Table 1. It was not possible to obtain information for peat soil because there is not a simple method for getting it's mechanical analysis, but it can be surmised that the organic matter is quite high.

Table 1

	% Sand	% Silt	% Clay
Chehalis	62.91	23.56	13.53
Sandy Soil	77.47	14.55	7.98

The chemical and physical properties of TBA which might relate to the adsorption and leaching behavior of this chemical in the soil were determined. Table 2 gives a summary of these determinations.

Table 2

Properties of TBA

1. Formula

2. Molecular weight   225

3. Melting point   115-120° C.

4. Solubility in:

    A. Water   7.6 gr/liter

    B. Cyclohexane   20.0 gr/liter

    C. Chloroform   180.0 gr/liter

5. p^H of saturated solution   1.70

6. Approximate ionization 4.8×10^{-2}
   constant
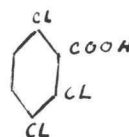
It was necessary to have some method of determining TBA in order to evaluate the amount adsorbed by soil and in determining the leaching behavior of this chemical. Since no chemical reactions were available, by which this compound could be conveniently determined for this study, it was necessary to use ultra-violet light absorption for determination. The light absorption spectra of TBA was determined with the chemical in water, cyclohexane, and chloroform. It was found that TBA absorbs only in the ultra-violet, exhibiting 2 maxima, one below 240 milli-microns and the other around 280 millimicrons. The

characteristic absorption spectra of TBA is presented in Graph 1.

The sharp maximum of TBA at 280 millimicrons, indicated the compound could be determined quantitatively by reading a solution at this wave length. Standard curves consisting of a plot of absorbancy versus concentration, were prepared by using a weighed amount of TBA made to volume in solution, and serially diluted to give the desired concentration. The standard curve obtained is presented for chloroform in Graph 2. The graph indicates it is possible to make quantitative determination of TBA in either of these three solvents.

The next problem was extracting TBA from a water solution into an organic solvent for quantative determination. Where a water solution of TBA had been shaken up with soil to determine the amount of adsorption of TBA on that soil, a turbid solution of suspended colloids resulted. It was impossible to get accurate readings of the concentration for TBA in such a solution. It was therefore necessary to extract the TBA into an organic solvent, in order to have a clear solution for the determination.

It was first necessary to determine which of the two solvents, cyclohexane or chloroform, would be the best

Graph 1

Absorption Spectra of
TBA in Chloroform

34

Graph 2   35

Standard Curve

TCB r: Chloroform

At 280 Å

Abs

Absorbancy

1.6

1.4   ⊙ ← 500

1.2

1.

.8

.6

.4

.2   ⊙ ← 100
                        50

            ⊙ ⊙

        50 100   200   300   400   500   PPm

Concentration in ppm
or Milligram per Liter
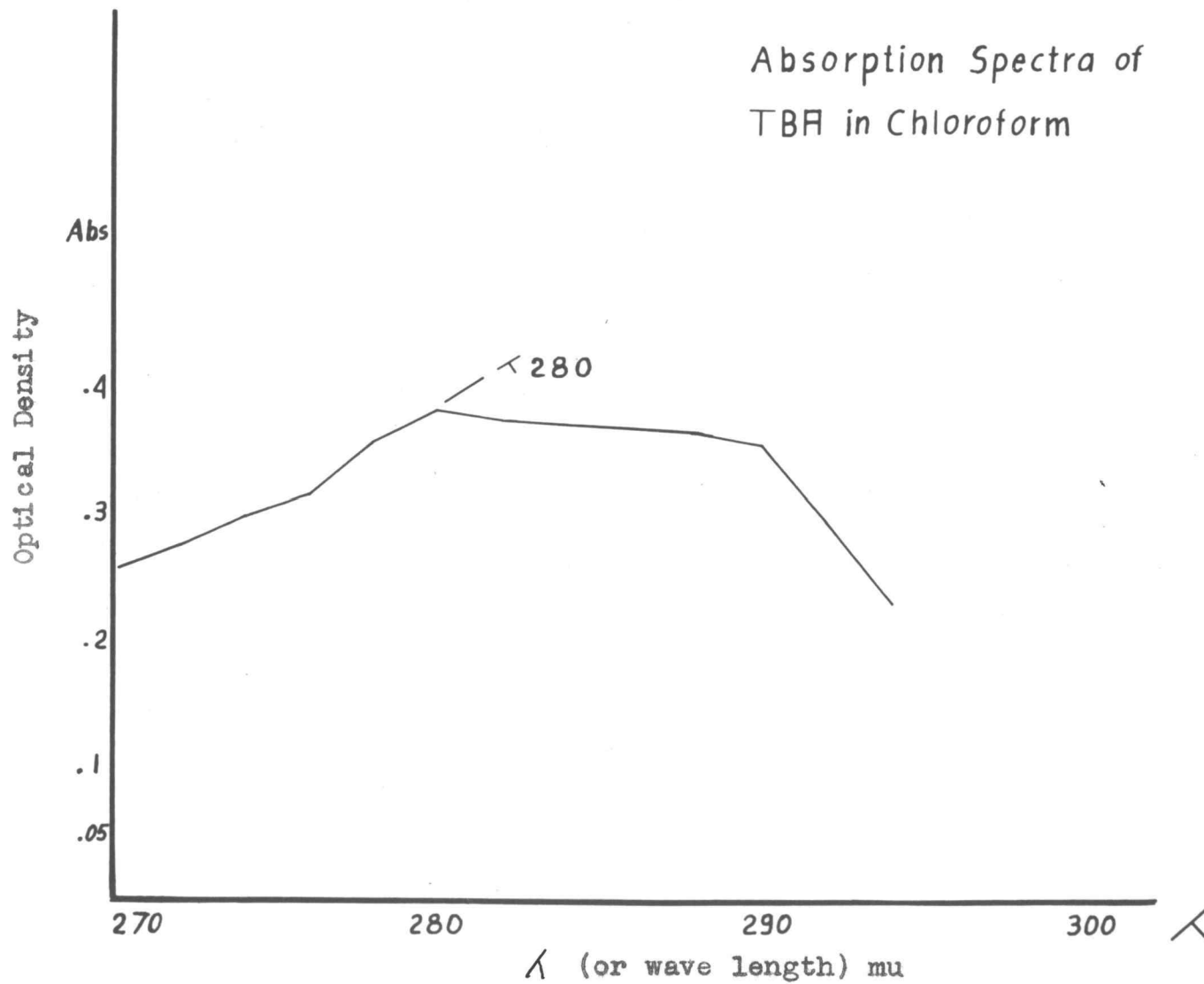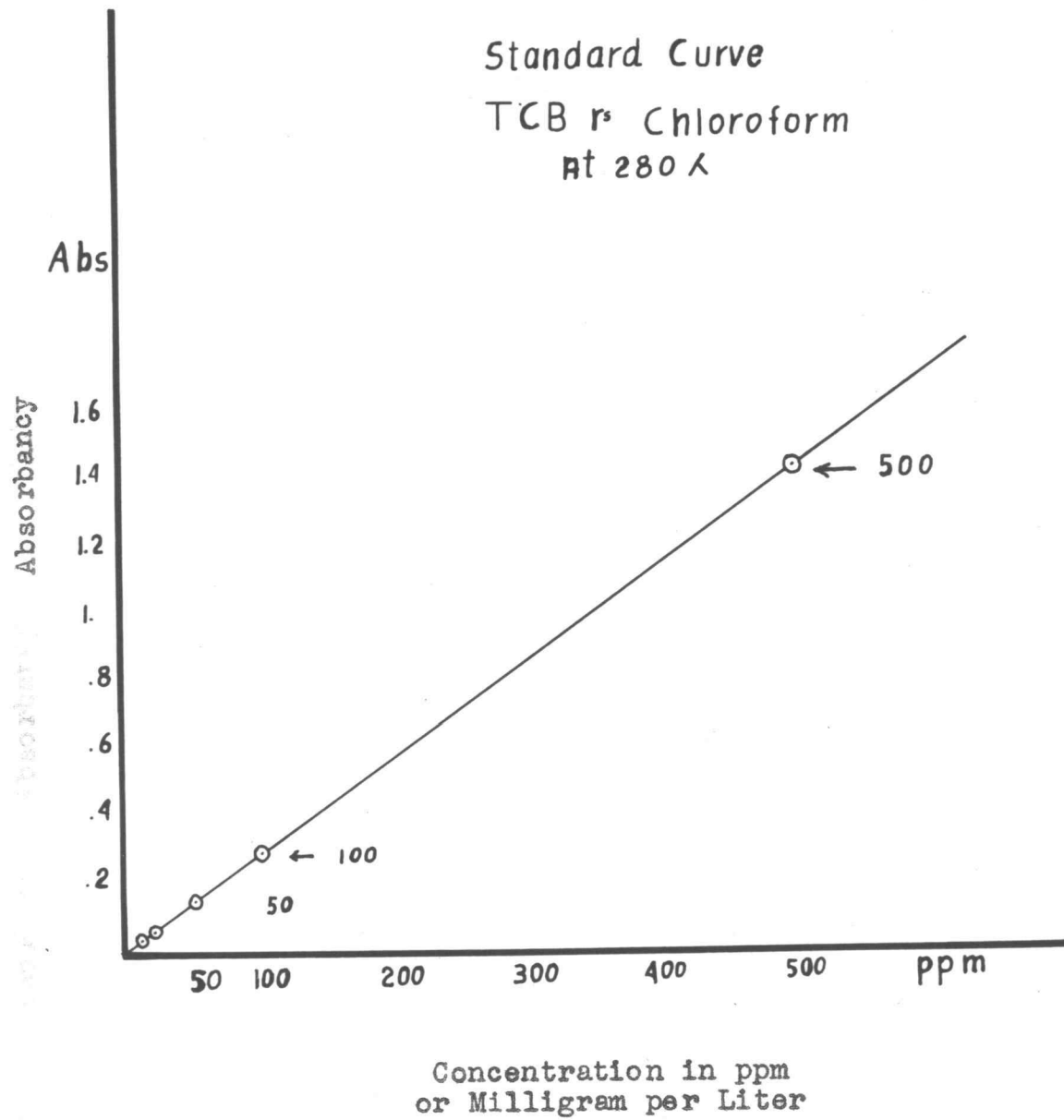
extractant for this purpose. A number of comparisons of
the two solvents were made, using TBA solutions of known
concentration. The result of these comparisons are pre-
sented in Table 3.

Table 3

Amount of TBA Extracted from Water
by Different Solvents

Samples	A. Chloroform		B. Cyclohexane	
	ppm Recovered	Percent Recovered	ppm Recovered	Percent Recovered
1	478	58.9	100	40.0
2	470	57.9	92	36.8
3	472	58.1	104	41.6
4	480	59.1	98	39.2

Average 58.5   Average 39.4

A. Original solution contained 810 ppm

B. Original solution contained 400 ppm

Determination by reading at 280 mu

The extractions reported in Table 3 consisted of shaking
a standard solution of TBA with twice it's volume of sol-
vent. In these comparisons single 50 milliliter extractions
were used with 25 milliliters of the solution. It is seen

by inspection of the table, that chloroform is a much
better solvent for this purpose. This would be expected
on the basis of the solubility of the TBA in the two
different organic solvents.

Since the single extraction with twice the volume of
organic solvent gave a recovery of only a little better
than 58% for chloroform, it was decided to investigate
the methods of extraction to see if recovery could not be
increased. The volume of extractant and standard solution
were held constant but instead of using a single extraction
the solvent was used in aliquots and single, double, triple,
and quadruple extractions were made. The results of this
study are presented in Table 4.

Table 4

Number of Extractions as a Factor in Recovery
of TBA from a 250 ppm. Water Solution

Times Extracted	Chloroform Amount	ppm Recovered	Percent Recovered
1	50 ml.	144	57.60
2	25-25	164	65.60
3	25-15-10	186	74.40
4	20-10-10-10	194	77.60

Triple extraction gave a much higher recovery than either the single or double extractions. The gain in efficiency of recovery for the quadruple extraction over triple extraction was much less than the gain from the other increments.

The extractions reported previously were based on a 2-minute hand shake with each aliquot of solvent. In order to determine if a longer shaking period might increase the efficiency of recovery, an aliquot of 25 milliliters of standard TBA solution and 50 milliliters of chloroform were put into a flask and placed in a mechanical shaker. Various lengths of time for shaking were employed, ranging from one-half hour to two hours. The recovery in each case is reported in Table 5.

Table 5

Shaking Time as a Factor
in TBA Extraction

Sample	Time of Shaking (Hours)	ppm Recovered	Percent Recovered
1	.5	60	51.0
2		48	41.0
3	1.0	40	34.0
4		46	38.0
5	2.0	80	67.0
6		42	35.0

Comparison of the data in Table 5 and Table 3 shows there is no advantage in mechanical shaking over hand shaking in percentage recovery. It would appear that shaking by hand in a separatory funnel gives better results than those achieved on a mechanical shaker.

Consideration of the chemical properties of TBA in relation to extraction suggested this chemical might be extracted best from an acid solution. Since TBA is a strong acid, there is not only the possibility of it reacting with any cation present in the solution, but also the high degree of ionization would result in a less efficient extraction. The purpose of acidification would

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be to repress the ionization of TBA and shift the equili-
brium of solubility in favor of the organic phase. To
test this theory, comparisons were made between the
efficiency of extraction of TBA from acidified and non-
acidified solution, using chloroform. These data are
reported in Table 6.

Table 6

Comparison of Extraction Efficiency of TBA
in Chloroform from Acidified and
Non-acidified Solution

| Sample | A. Acidified | | B. Non-acidified | |
	ppm Recovered	Percent Recovered	ppm Recovered	Percent Recovered
1	744	97.8	480	59.1
2	730	96.0	478	58.8
3	722	95.0	472	58.1
		Average 96.2		Average 58.6

A. The acidified solution contained 760 ppm.

B. The non-acidified solution contained 810 ppm.

Acidification markedly assisted in the recovery of TBA from a water solution. In the case of the acidified extraction, 96% of the TBA was recovered, whereas in the non-acidified portion, 58.6% of the TBA was recovered. The percentage recovery from the non-acidified portion gave very close duplication to the percentage recovery found in Table 3, which had been carried out under comparable conditions.

It was necessary to determine how acidification versus non-acidification compared in the extraction of TBA from a solution that had been shaken with soil. TBA, being a strong acid, would react with cations of the soil, such as calcium, magnesium, sodium and potasium, to form salts which would not be extracted from the solution without acidification. Such a study was carried out and is reported in Table 7.

Table 7

Adsorption of TBA from Non-acidified
Versus Acidified Chehalis Soil Solution

Samples	A. Acidified		B. Non-acidified	
	γ Adsorbed per Gram of soil	% Adsorbed	γ Adsorbed per Gram of soil	% Adsorbed
1	8,762.4	96.7	4,928.0	54.4
2	8,750.0	96.5	4,937.8	54.5

From a soil solution containing 9.060 γ/gr. of soil

There was almost a two-fold difference in recovery between the acidified and non-acidified solutions. The procedures in this study consisted of equilibrating 100 milliliters of TBA solution and 40 grams of soil, filtering off the soil, and centrifuging the supernatant solution. Aliquots of the clear solution were taken for extraction. In this manner the determination would recover only the TBA in solution. The behavior evidenced in the recovery study indicates TBA does react with the soluble cations of the soil solution.

To study the leaching behavior of TBA, it was necessary to find a method to determine the TBA in soil, and make a quantative recovery of TBA in each fraction of the soil columns. An attempt was made to recover TBA from the dry soil by the use of exhaustive extraction. Six place fat extractors were used for exhaustive extraction of soil containing TBA, by use of two different solvents. The results of this study are reported in Table 8.

Table 8

Amount of TBA Extracted from Soil
by Different Solvents

| Samples | A. Chloroform | | B. Cyclohexane | |
	ppm Recovered	Percent Recovered	ppm Recovered	Percent Recovered
1	105	122.5	30	75.2
2	102	115.0	28	68.7
3	94	95.0	29	72.5
Blanks				
4	60		12	
5	50		9	
6	57		7	

25 grams of sandy soil containing 80 ppm. TBA were used. The average amount recovered by blank was used as a correction factor.

The data shows an extremely high recovery with chloroform. A difficulty was experienced with this solvent, since the blank extracted from an untreated soil, was both high and erratic. Cyclohexane gave only slightly better than 70% recovery, but the blanks were low and consistent. For this reason cyclohexane was selected as the solvent for extraction of the soils in the leaching study.

Since TBA was being leached into the soil by water,

there was a possibility of the TBA reacting with the cations of the soil, as well as being adsorbed. A study to determine if release of the TBA could be achieved by acidifying the soil was undertaken. Samples of soil, corresponding to the amount used for extraction, were tested to determine the amount of sulfuric acid required to lower them·to a p^H of 2. Samples containing a known amount of TBA were then exhaustively extracted after acidification with sulfuric acid and drying. Table 9 presents the results of this study.

Table 9

Extraction of TBA from Acidified
and Non-acidified Soil Containing
80 ppm -- Cyclohexane as a Solvent

	Percent TBA Recovered	
Sample	A. Acidified Soil	B. Non-acidified Soil
1	90.4	75.2
2	86.2	68.7
3	98.8	72.5

A. Average 91.8

B. Average 72.1

The addition of acid to the soil gave enhanced re-
covery of TBA, and consequently this procedure was adopted
for extraction of TBA from the soil. The adsorption of
chemicals applied to a soil is of major importance to
their subsequent behavior since when the chemical is ad-
sorbed, it's herbicidal action may be impaired. The
leaching behavior of chemicals is directly related to
the adsorption bond energy. Thus, investigation of the
adsorption of the chemical by the soil fractions was
deemed important. Adsorption of TBA by the three dif-
ferent soil types was investigated. Three different con-
centrations of TBA solution were equilibrated against a
fixed weight of soil. In the case of the mineral soils,
40 grams of soil were used in 100 milliliter solutions
which contained 76 ppm. and 3800 ppm. of TBA. With the
peat soil, 8 grams were used with the 100 milliliters of
solution. Following filtration of the soil from the
solution and clarification by centrifuging, an aliquot of
the supernatant liquid was acidified and extracted with
chloroform. The data were then calculated to determine
the micrograms of chemical adsorbed per gram of soil. The
coefficient of variation was calculated for the concen-
tration of chemical for each soil type. The data thus ob-
tained are presented in Table 10.

Table 10

Adsorption of TBA in Three Soil Types

| | | | TBA | Acidified Soil Sol'n | |
| | | | Run 1 | Run 2 | |
Soil Type	ppm Solution		ɤAdsorbed per Gram of Soil	ɤAdsorbed per Gram of Soil	C.V.
Sandy *40 gms*	76	*190*	--	--	--
"	760	*1900*	265.1 269.7	255.6	3.2
"	3800	*9500*	1348.6 1336.8	1348.6	.30
Chehalis loam *40 gms*	76	*190*	31.3 38.1	35.8	2.2
"	760	*1900*	838.8 875.0	877.3	1.6
"	3800	*9500*	2343.8 2049.0	1935.6	8.9
Peat *8 gms*	76	*950*	421.0 398.8	365.0	8.1
"	760	*9500*	3762.5 3875.0	3751.3	12.8
"	3800	*47000*	9520.0 9295.0	9418.7	.8

The variation in the ability of different soils to adsorb TBA is apparent from the data presented. Since the colloid content and organic matter content of these soils increases progressively from sandy to Chehalis to peat soil, the correlation of adsorption with colloid and

organic matter content is indicated. The peat soil, with a high organic matter content and a large colloidal surface for adsorption, adsorbed about seven times the amount of chemical at the highest concentration, as compared to the sandy soil. The maximum percent adsorbed by the soil approached only 40 percent of the available TBA. Many other chemicals, particularly those of low water solubility, will be adsorbed to extents approaching 70 to 80 percent of the available chemical in a saturated solution. A comparison was made between the adsorption of TBA and 2,4-D by Chehalis soil. 2,4-D is also an acid but has a much lower water solubility and is quite strongly adsorbed by soils. The absorption spectra of 2,4-D determined for the purpose of establishing a method of measurement, is presented in Graph 3, and the standard curve prepared using the absorption maxima as the point of reading is given in Graph 4. Table 11 presents the comparison of the amount of 2,4-D adsorbed compared with TBA.

Graph 3

Absorption Spectra of
2. 4-D acid in Chloroform
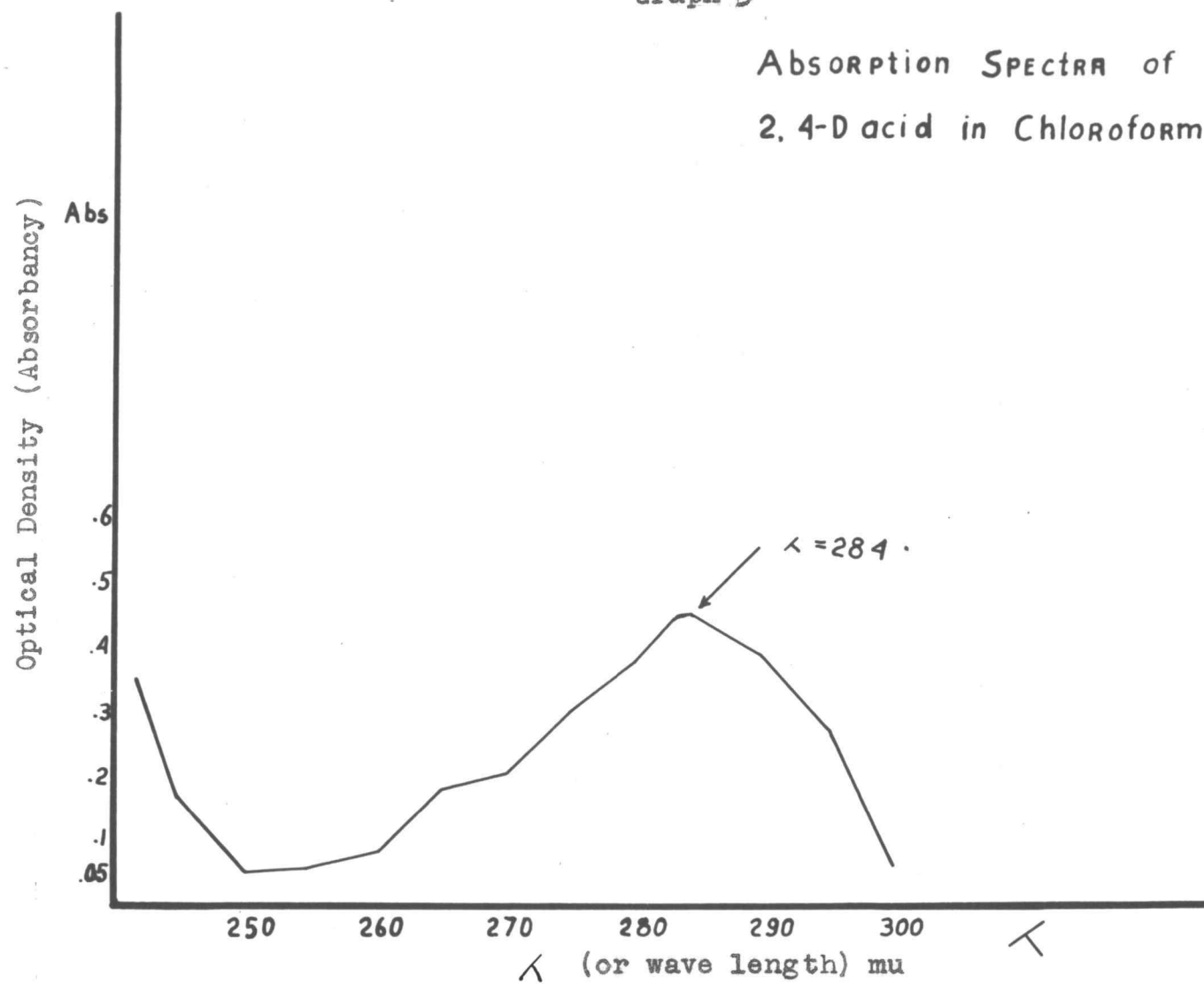
Graph 4

Standard Curve of

2,4 D acid in Chloroform

$\curlywedge = 284$

Abs

Absorbancy

Concentration in ppm

49
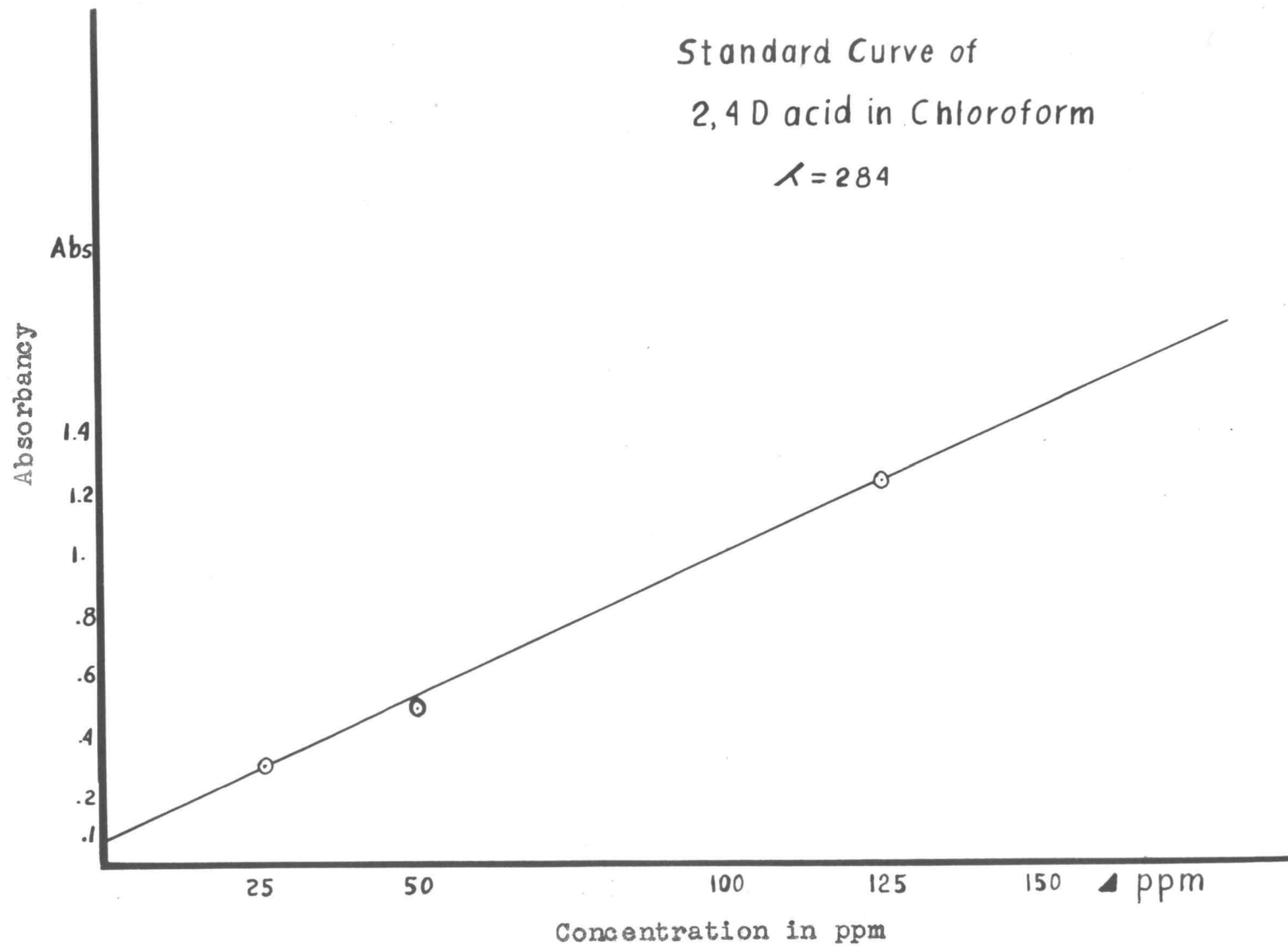
Table 11

Comparison of the Adsorption of TBA and 2,4-D from Chehalis Soil

Sample	Rate	TBA ppm in Solution	A. TBA γ Adsorbed per gram of Soil	Percent Adsorption	2,4-D ppm in Solution	B. 2,4-D γ Adsorbed per gram of Soil	Percent Adsorption
1	Light	76	31.3	16.5	20	--	100
2			38.1	20.1		--	100
3			35.8	18.4		--	100
4	Medium	760	838.8	44.1	100	164.8	65.9
5			875.0	46.1		169.7	67.9
6			877.3	46.2		172.8	69.1
7	Heavy	3800	2343.8	24.7	500	1139.9	91.2
8			2049.0	21.7		1132.2	90.6
9			1935.6	20.4		1134.7	90.6

A great deal more 2,4-D than TBA was adsorbed by the Chehalis soil. This would be expected in part from the solubility behavior of the two chemicals. The TBA has a solubility of about 7000 ppm., 2,4-D has a solubility of around 700 ppm. Other factors, such as the chemical structure, affect adsorbability of a compound so that differences between the two chemicals cannot be compared directly. The data in Table 11 indicate that adsorption of TBA is not particularly great, and therefore TBA should be quite mobile in the soil solution.

The movement of TBA in the soil is important to the action of this chemical. Leaching or movement in the soil may be a means by which the chemical is lost, and the herbicidal efficiency thus reduced, but it may also be important in the action on the roots of deep rooted perennial weeds. In dealing with deep rooted perennial weeds, the mobility is needed to get the chemical in contact with the deeper root system. The leaching behavior of this chemical was therefore studied.

It is not possible in the laboratory to exactly duplicate the leaching conditions encountered in the field. Leaching studies in the laboratory can be used only to indicate principles and patterns rather than getting exact information. Study of the leaching behavior

of TBA was undertaken to elucidate the principles. The
following factors in relationship to leaching behavior of
TBA were studied:

A. The influence of rate of TBA application on
leaching.

B. The relationship of soil type to leaching.

C. The relationship of water content of the soil
to leaching.

D. The effect of water cycles or intensity of
moisture on leaching.

The first factor to be evaluated was the influence of
the rate of chemical application on the depth of pene-
tration of the chemical. With a light rate of chemical
application, penetration is assumed to be poor, and with
increasing amounts of chemical, more and more of the com-
pound attains a greater depth in the soil profile. In
this experiment soil columns were set up, employing a
12-inch column as described under materials and methods.
The soil used was Chehalis soil, air dry, to which was
added just sufficient moisture to bring the entire column
to field capacity. The water was added after the chemical
had been placed on the surface of the soil, and was
introduced into the column over a period of four hours.
Three rates of chemical application were compared. The

results of this experiment are presented in Table 12.

Table 12

Depth of Penetration as a Function
of Rate of Application

Chehalis Soil

Column Section	Inches Deep	γ/Column	Run 1 % of Total	Run 2 % of Total
1	0-3	760	--	--
2	3-6		20.4	17.4
3	6-9		20.4	--
4	9-12		59.2	82.6
1	0-3	1,520	15.4	16.7
2	3-6		10.5	1.7
3	6-9		26.8	47.2
4	9-12		47.3	34.4
1	0-3	3,040	20.1	19.0
2	3-6		12.3	18.2
3	6-9		31.5	31.0
4	9-12		36.1	31.8

If the amount of chemical applied to the surface of
the soil determined the depth to which the chemical would
penetrate, the lowest rate of application, which was one-
fourth the heaviest rate, should have little chemical in
the fourth section of the column. This was not the case,
as shown in Table 12. On a percentage basis, more chemi-
cal was found in the lowest section of the column with a
light rate of application than with higher rates. In

terms of absolute amount, more micrograms of chemical
were found in the fourth section at the two heavy rates,
compared with the light. This indicates depth of pene-
tration is independent of the amount of chemical applied,
but the absolute amount of chemical penetrating into the
soil is influenced by the amount applied.

The next leaching problem to be investigated was the
influence of soil type on the rate of chemical movement.
Soil columns were prepared as described. A single rate of
application for the chemical was made to each column. In
one instance dry soil was used and a sufficient amount of
water was added to bring the soil of the column to field
capacity. In this case, difficulty was encountered in
analyzing the peat soil for the presence of TBA. This
was great enough to invalidate the data. The other por-
tion of this experiment involved bringing the soils to
field capacity prior to application of the chemical.
After the chemical had been applied, each column was
leached with 3 inches of water. These data are reported
in Table 13.

Table 13

Leaching as a Function of Soil Type

Soil Type	Column Section	Inches Deep	A. Dry Soil % of Total	B. Field Capacity % of Total
Sandy	1	0-3	--	--
	2	3-6	--	--
	3	6-9	--	59.3
	4	9-12	100.0	41.7
Chehalis	1	0-3	22.4	21.1
	2	3-6	--	21.2
	3	6-9	24.8	40.5
	4	9-12	52.8	17.2
Peat	1	0-3		58.0
	2	3-6		22.5
	3	6-9		15.7
	4	9-12		3.8

A number of comparisons may be made from the data in Table 13. When the soil profiles were brought to field capacity, the depth of TBA penetration was approximately the same. The proportional amount of TBA recovered as depth increased was greater if the soil texture was coarser. This appears to support the contention that depth of penetration is independent of rate of application and is a function more of the movement of the water.

Comparisons where the soil was brought to field capacity first show the velocity of TBA movement was

reduced. The absolute amount of chemical found in the different sections of the column decreased as the soil moisture increased. This would be a consequence of the slower rate of water penetration into the moist soil. Comparisons may also be made of the effect of soil type on the movement of TBA. In the sandy soil, penetration was rapid and deep. In the Chehalis soil it was slowed with the maximum concentration found in the third section. With the peat soil, the maximum concentration was still in the first section of the column and only a small percentage had reached the fourth section of the column. Since some chemical was found in the fourth sections of the columns of all three soil types, the indication is that the chemical moved freely with the penetration of water. The soils with the greater adsorption capacity for TBA reduced the rate of movement.

Theory of the leaching process suggested that as the intensity of water penetration decreased, even though the total amount of water over a period of time were the same, redistribution of the chemical in the soil profile would occur by the diffusion process. Columns were set up with Chehalis soil to measure the effect of water cycles on the leaching process. The first set of columns had a total of 6 inches of water introduced over a 4-hour

period. In the second group, 2 inches of water were
applied each day, until a total of 6 inches had been
introduced into the columns, and in the third group,
one inch of water was applied daily to the column over
a period of 6 days, to give a total of 6 inches of
moisture. The data obtained in terms of percentage dis-
tribution in the different sections of the column is
presented in Table 14.

Table 14

Leaching as a Function of Water Cycle

Column Section	Inches Deep	A % of Total	B % of Total	C % of Total
1	0-3	19.8	32.5	38.8
2	3-6	33.0	28.5	15.1
3	6-9	16.1	19.5	27.8
4	9-12	31.1	19.5	18.3

A. 6" of water over one period of time

B. 2" of water per day until complete 6"

C. 1" of water per day until complete 6"

This table shows where water intensity is high
(Treatment A), the chemical is rapidly moved to the lower
depths of the column, but as the water intensity is re-
duced, the distribution pattern changes. In the cycles
labeled B and C, where the water penetration intensity had

been reduced, a much higher concentration of chemical is
to be found in the top section of the column. The in-
dications from these two columns is that redistribution
of the concentration is brought about by diffusion. This
behavior is one that would be expected in the field where
rainfall occurs intermitently and the total rainfall does
not come at one time.

DISCUSSION

It is now a well established fact that the behavior of a chemical in the soil is, to a large measure, determined by the physical and chemical properties of the compound. Such factors as water solubility, volatility, ability to complex and reactivity, all interact with factors of the environment to determine the length of residual life of the chemical and the availability for herbicidal action.

It will be noted from the information in Table 2 that TBA is a strong acid. This fact should have considerable significance in the possibility of TBA reacting with various cations in the soil, to form metalic salts. The formation of these salts should, as a consequence, increase the leachability of TBA, and since salt formation would be in competition with adsorption for TBA, it should mean that less of the chemical will be adsorbed than if it were a weaker acid. Another fact to be noted in this table is the relatively high water solubility of this compound. Inasmuch as benzoic acid itself has a solubility only slightly higher than this, the solubility is somewhat surprising. Normally, one expects that as chlorination of an aromatic compound increases the water solubility of the chemical is markedly depressed.

The processes going on in the soil, such as adsorption, leaching, volatilization, salt formation, and reaction with soil components are very important in the use of herbicides applied to the soil for weed control. An understanding of these factors and their importance is necessary so that a herbicide may be used most effectively. This includes estimate of the residual life for a chemical. It is now known that the behavior of a chemical in the soil is markedly influenced by the interaction of it's chemical and physical properties with the various factors of the environment. The chemical TBA has come into considerable use as a soil active herbicide. It has shown particular effectiveness in the control of many of the deep rooted perennial weeds. It is of importance, therefore, that we know something about the factors that influence the effectiveness of this material, as well as attempt to obtain some sort of explanation for the particular effectiveness of the chemical against the deep rooted perennial plants. Knowledge of such factors as adsorption, leaching, and some of the chemical properties of the compound, would be of considerable value in interpreting results with this chemical.

In this study, it has been shown that TBA is a strong acid of appreciable water solubility. From these

observations, it is deduced that the chemical should react to form water soluble metallic salts, and this, coupled with the high water solubility, should result in ready mobility of the chemical in the soil profile. This was found to be the case. Compared with 2,4-D, the absorption of TBA was much less. The 2,4-D is quite strongly bound by soil colloids, and has low mobility in the soil compared with TBA.

In studies on recovery of TBA from the soils, it was found that TBA demonstrated an appreciable volatility during the drying process. This is probably due to an appreciable vapor pressure of the chemical and it's volatility with steam or water vapors coming off the soil. It would appear, therefore, that this might be an important factor in the loss of this chemical from the soil surface, particularly in the case of a moist soil. It is possible that partial loss could occur by volatilization or steam distillation under circumstances where the rate of evaporation from the soil was great.

The leaching studies demonstrated the movement of TBA in the soil tended to follow water flow lines. In addition, diffusion tended to redistribute the chemical in the soil profile. Such a redistribution has been found with IPC. This could mean that even though the chemical

had been distributed in the soil profile by leaching, it could concentrate near the surface under the influence of air movement and high air temperatures. An appreciable amount of water evaporating from the soil surface would tend to cause this concentration, as occurs with other soluble salts. This would subject the TBA to possible loss via steam distillation or volatilization. The tendency of TBA to form salts with cations found in the soil would attenuate this loss.

Consideration of the chemistry of TBA would suggest that in comparison to other compounds, it would not be strongly adsorbed by soil colloids. This was found to be the case, although the usual pattern of increased adsorption on heavier soil types, or with increasing organic matter content as found for other herbicides, was also true for TBA.

Certain factors are already known to have a bearing on leaching behavior of chemicals; thus, leaching is thought to be slower in a heavy soil, as compared to a light soil. Also, it is felt, although it has never been demonstrated unequivocally, that the actual leaching movement of chemicals in soil tends to follow the water flow lines. It was mentioned, in connection with the adsorption study, that the adsorption of the chemical by

the soil is also an important factor in determining the
leaching behavior of the material in the soil.

TBA appeared to follow the theoretical principles
of the wave movement of the maximum concentration of
chemicals. This theory suggested that penetration of the
chemical front into the soil profile should be indepen-
dent of the amount of chemical applied to the soil surface.

Consideration of the equation given for the depth of
maximum concentration of a chemical as a function of
applied moisture suggested that the depth of penetration
of a chemical into the soil should be independent of the
amount of chemical applied to a surface. The rate of
chemical, then, only influences the absolute amount of
chemical found at any soil depth, as indicated by this
consideration. In further consideration of the leaching
problem, it was felt that diffusion of the chemical in
the capillary moisture, should be an important factor in
causing equilibration of the distribution of the chemical
in the soil profile. It is recognized that if a con-
tinuous front of water is moving through the soil, the
chemical should be carried along with that, but when the
water is no longer moving, then the distribution forces
would come into play, and the chemical equilibrate as to
concentration.

The failure of other investigators to demonstrate this is apparently due to the limitations of the detection methods used by them. The failure to demonstrate this in other studies probably is due to the fact that bioassays were used to detect the chemical. Adsorption of chemical by the soil reduced the concentration of chemical in soil solution available for herbicidal action to the point where it was not detected by these assays. It thus appears that the inferences drawn from the equation involving the movement of maximum concentration, are valid and supported by the data reported here.

In this study employing chemical techniques, it was found that TBA does penetrate the soil profile more or less independently of the amount of chemical applied to the surface of the soil. However, this should be distinguished from the total amount of chemical, or maximum concentration of chemical in the soil profile. There, as the rate of chemical application increases, the amount of chemical to be found at any depth in the soil profile, also increases.

Another interesting observation in the leaching behavior of TBA is that with an amount of moisture penetrating in the soil, sufficient to fill dry soil to field capacity, the depth of penetration of chemical is about

equal in the two different types of mineral soil. Such
finding is supported, in a large measure, by the behavior
of chemical compounds in paper chromatography, where with
a given solvent system, the Rf value will be about the
same on a number of different papers. However, the dis-
tribution of the chemical in the soil profile, as to
absolute amounts, is definitely a function of soil type
as would be required from consideration of the adsorption
bond energies, which increase as soil type gets heavier.

This again is a necessary consequence of the possi-
bility that the chemical is following the water flow lines
of the soil. Also, it was found that the amount of chemi-
cal penetrating the soil profile decreased as the water
content of the soil profile increased. This is inter-
preted as indicating that the water penetration is markedly
reduced, and hence less chemical would appear in different
segments of the soil profile. This is a marked contrast
to the theory held by Upchurch (29, p. 329). While the
compound used by Upchurch was a substituted urea, and the
one used here is a soluble acid, it does not seem reason-
able that the two chemicals would be subject to two
different chemical principles.

This study suggests that the soil behavior of
chemicals is following well defined laws and principles

that are just now being discovered. Certain predictions had been made on the basis of the chemistry of TBA and when these predictions were tested, the results of the experiment and the predictions were in agreement. It would seem, therefore, on the basis of the findings presented that the behavior of TBA under varying conditions could be predicted to a close approximation.

It is recognized, of course, that this work should be repeated to increase the validity of the inferences that may be drawn, but the very close agreement found in comparing results of replicate soil columns, increases one's confidence in the data presented.

Moreover, comparisons of results obtained with biological assay to those obtained by chemical means should be made.

The loss of herbicidal activity in the soil involves not only loss by adsorption and leaching, but by volatilization and microbiological breakdown as well. Further investigation of the soil behavior of TBA should include a study of these latter two factors, so that more accurate predictions of field performance may be made.

SUMMARY AND CONCLUSIONS

The study presented here was concerned with the soil behavior of the herbicide TBA. The first phase of the investigation involved measuring some of the properties of TBA, since these properties are known to influence the soil behavior of chemicals. In addition, a method for the quantative determination of TBA in solution was developed. The methods were employed to determine TBA in both the adsorption and leaching studies.

The physical and chemical properties of TBA, such as solubility in different solvents, the efficiency of extraction by different solvents from either water or soil solution, as well as from the soil itself, were studied, since these properties might relate to the adsorption and leaching behavior of this chemical in the soil.

A study of adsorption of TBA by the soil was conducted. The chemical was allowed to equilibrate with 3 soil types at different rates, and the amount adsorbed by soil was then calculated. A comparison was made between TBA and 2,4-D as to their adsorption on Chehalis soil.

Some factors affecting the removal of TBA from soils by leaching, such as the influence of rate of application,

the relationship of soil type, the effect of water content
of the soil and the effect of water cycle, as influencing
leaching, were studied. From the results obtained in this
work, it may be concluded:

1. TBA has a much higher solubility in water than
has been assumed. The ionization constant indicates that
it is a strong acid. These properties are shown to have a
direct bearing on the soil behavior of the chemical. The
high water solubility together with the tendency of TBA to
form salts because of its acid strength, makes for poor
adsorption and hence high mobility in the soil.

2. TBA was found to have an appreciable volatility
which may have considerable significance in its loss from
soil surfaces.

3. The adsorption of TBA by soil increases as clay
and organic matter content of the soil increases. However, TBA is not as well adsorbed as 2,4-D.

4. The depth of penetration into a soil profile by
a chemical as a result of leaching is independent of the
amount of chemical applied. The amount in terms of concentration, however, relates to the rate of application.
This type of behavior is required by the leaching theory.

5. The amount of chemical leached by an amount of
water required to bring the soil to field capacity

decreases with heavier soil types. The depth of penetration remains unaffected.

6. The penetration of a chemical into the soil profile follows the lines of water flow. The amount of chemical leached is a function of the amount and rate of water percolation.

7. The amount and intensity of rainfall influences leaching. The same amount of water over a short period of time leaches more chemical into the soil than the same amount over a period of time.

8. Diffusion of the chemical causes redistribution of the TBA in the soil profile.

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