

- (12) Laurie, A., and Kiplinger, D. C., "Commercial Flower Forcing," 5th ed., Philadelphia, Blakiston Co., 1948.
- (13) Lignon, W. S., and Pierre, W. H., *Soil Sci.*, **34**, 307-21 (1932).
- (14) Moser, F., *Soil Sci. Soc. Am. Proc.*, **7**, 339-44 (1942).
- (15) Ohio Agr. Expt. Sta., *Bull.* **381** (1924).
- (16) Peech, M., and English, L., *Soil Sci.*, **57**, 167-95 (1944).
- (17) Piper, C. D., "Soil and Plant Analysis," New York, Interscience Publishers, 1950.
- (18) Ririe, D., and Toth, S. J., *Plant Sci.*, **73**, 1-10 (1952).
- (19) True, R. H., *J. Am. Soc. Agron.*, **13**, 91-107 (1921).
- (20) U. S. Regional Salinity Laboratory,

"Diagnosis and Improvement of Saline and Alkali Soils," L. A. Richards, ed., 1947.

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SOIL EFFECTS ON HERBICIDES

Adsorption of 3(*p*-Chlorophenyl)-1,1-dimethylurea As a Function of Soil Constituents

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In a study of the rate of adsorption of 3(*p*-chlorophenyl)-1,1-dimethylurea (CMU) on different soil types, a method was developed for determining the amount of CMU adsorbed on various materials. Twelve different soils were tested and the absorption was correlated with mechanical composition. The results indicate that there is very high adsorption of CMU on organic matter and a significant rate of adsorption on inorganic clay particles.

THE HERBICIDE 3(*p*-chlorophenyl)-1,1-dimethylurea (CMU) has been reported to be less effective on a heavy soil than on a light soil and more persistent on the heavy soil (5). As this material is being used widely as a soil sterilant, such considerations are of practical importance.

It was proposed that this difference in activity and persistence in different soil types might be due to physical adsorption of the CMU molecule on the soil particles.

Therefore, an experiment was conducted to observe the difference in the quantity of adsorption on various soils and to correlate this adsorption with certain soil properties.

Experimental Methods

The soils used in this study were selected because of their varying composition. Asbestos, cotton, dicalite, kaolin, activated carbon, sawdust, and straw were also used as adsorbates in an attempt to determine whether adsorption of CMU is due to a particular type of adsorbing surface.

After many procedures had been tried the following method was developed to measure the quantity of adsorption.

A 10-gram sample of air-dry soil (except for the muck soil, where 1 gram was used) was placed in a 50-ml. plastic centrifuge tube with 25 ml. of 200 p.p.m.

CMU solution, and agitated periodically for 0.5 hour. Similarly, lesser amounts of the highly adsorptive materials were used in the determination. Preliminary results indicated that equilibrium had been attained in this period of time. The tube was then centrifuged on a size 2 International centrifuge at an acceleration of 656 times gravity. After the centrifuge period of 0.5 hour, the supernatant liquid was clear. A 10-ml. aliquot was removed from the supernatant liquid and diluted to 50 ml. in a volumetric flask. The CMU in a 2-ml. portion was determined according to the micro-quantitative acid hydrolysis procedure outlined by Lowen and Baker (6).

The amount of CMU that was not recovered was considered to be adsorbed. The pH was determined on a Beckman pH meter (7). The organic matter was determined according to the dichromate reduction method (7), and the moisture of each soil sample was determined gravimetrically, so that all calculations could be made on a dry weight basis (7). On each soil a mechanical analysis determination was conducted according to the procedure outlined by Bouyoucos (2), with the modifications suggested by Tyner (9) and Kilmer and Alexander (4). The correlation coefficient was calculated to obtain the relationship between the amount of CMU adsorbed and the soil properties that were determined (8).

Results and Discussion

The amount of CMU found to be adsorbed by the various soils and other substances and the properties of the soils as determined by the methods indicated are summarized in Table I. The figures presented represent an average of two determinations within a limit of precision of $\pm 1.34\%$. The adsorption study reported was carried out under one set of experimental conditions with no attempt to determine the adsorption isotherm. However, this is what would be encountered in a field application of a given rate of the chemical. While this does not permit exact quantitative comparison of the amount of chemical adsorbed, it provides a basis for estimating the relative readiness with which the soil adsorbs the material and the probable comparative tenacity with which the chemical is held. The amount of adsorption on the other substances is reported in Table II.

The correlation coefficients that were calculated are recorded in Table III.

From the data presented in Table II it is evident that CMU is readily adsorbed by organic substances such as Norite, sawdust, and straw, but not on cotton, which is also organic.

A correlation of pH, per cent silt, and per cent clay with the amount of CMU adsorbed is not significant. However, a correlation of all other properties that were determined with the amount of adsorption is highly significant. It is

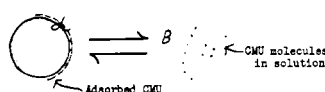
Table I. Analysis of Soils Used in This Study

No.	Soil	CMU Ad- sorbed γ/G .	pH	OM, %	Silt, %	Clay, <2 μ , %
1	Sand soil	23	7.60	0.9	19	5
2	Deschutes coarse sandy loam	24	7.08	1.7	35	15
3	Newberg fine sandy loam	21	6.26	1.5	34	19
4	Ritzville fine sandy loam	23	6.90	1.7	35	15
5	Chehalis loam	33	6.94	2.8	36	24
6	Palouse silt loam	237	6.14	3.5	68	18
7	Dayton silty clay loam	21	5.87	4.1	57	32
8	Aiken clay loam	90	5.92	1.3	37	53
9	Willamette clay loam	44	6.78	4.8	55	34
10	Cove clay	41	6.25	3.7	38	49
11	Muck soil	3453	5.55	83.3	Cannot	determine
12	Wapato silt loam	39	5.95	3.2	62	27

obvious that the percentage of organic matter is very highly correlated with the amount that CMU is adsorbed in the soil, but that there is also an inorganic adsorption.

In preliminary experiments to determine the effect of adsorption on the biological activity of CMU, samples of the various soils were permitted to adsorb the chemical and after washing to remove the nonadsorbed chemical, seeds were planted in the soils. The soils having the highest affinity for CMU reduced the effectiveness of the chemical on rye grass (*Lolium multiflorum*). This was evidenced by the longer time required by the plant to show symptoms of CMU toxicity on these soils as compared to soils with lower affinity for CMU.

Consideration of the problem leads to a physical picture somewhat as follows: In a system of CMU solution (aqueous) and adsorbing surface, the chemical would be found in the adsorbed phase (phase α) in dynamic equilibrium with the CMU in the aqueous phase (phase β).



Because the CMU is adsorbed, it is apparent that the "potential" μ (β) of the CMU in solution is different from that on the adsorbed surface.

$$\mu_{\alpha} \neq \mu_{\beta}$$

The potential of the CMU in solution is given by

$$\mu_{\beta} = \mu_{\beta}^{\circ} + RT \ln C_{\beta}$$

The potential of the CMU on the adsorbing surface will include surface energy terms, as shown by the following relationship;

$$dG^{\alpha} = -SdT - Ad\sigma + \sum \mu_i dn_i^{\alpha}$$

However, in this case, the interest lies in examining the influence of concentration in the aqueous phase. It is possible

to include this term in the "potential" term of the adsorbed CMU.

$$\mu_{\alpha} = \mu_{\alpha}^{\circ} + \Gamma d\mu$$

This reduces the consideration to the relation

$$\mu_{\alpha} = \mu_{\beta}^{\circ} + RT \ln C$$

whence

$$\frac{\mu_{\alpha} - \mu_{\beta}}{RT} = \ln C$$

The "free enthalpy" or driving force, G , of a reaction is given by $G = H - TS$, taking the partial differential of G with respect to the mole fraction, n_i , of component i

$$\frac{(\partial G)}{(\partial n_i)PTn_i} = \mu_i$$

where

- R = gas constant (1.987 cal. mole⁻¹)
- T = absolute temperature
- S = entropy
- Γ = surface concentration
- A = area
- C = concentration
- H = internal heat
- \ln = natural logarithm
- σ = surface tension

The term $\ln C$ tends toward a constant value and thus any disturbance causing it to change will result in a change of equilibria.

However, as the sorbing forces increase, it is to be expected that they will counteract μ_{α} and thus the material will be more tightly bound in phase α . The consequence of this is that the "biological activity" of the chemical in the soil will be decreased. The validity of this conclusion is attested to by the results of the above-mentioned trial. It may be deduced that an increase in extent of phase β will result in a greater amount of chemical in solution. This would provide a greater exposure of the plants to the toxicant with a resultant increase in effectiveness of the treatment, even though maximum concentration had not been achieved. Furthermore, it should

be possible by evaluation of the equilibrium concentration to assess the variation of sorbing energy with various surfaces.

Summary and Conclusions

A study of the amount of CMU adsorbed by various soils and other adsorbing surfaces showed that organic matter has considerable affinity for CMU. A correlation coefficient of 0.991 was found for the relationship between the amount of CMU adsorbed by the soil and the organic matter content. There is a statistically significant correlation between adsorption and the amount of clay in the soil.

On thermodynamic grounds it appears that ample moisture (but not sufficient to cause leaching) is required to overcome the problem of loss of effectiveness due to adsorption. However, in the cases of soils where the energy of sorption is greater than the "escaping tendency," the material may tend to remain in the soil a longer time than usual.

In the use of CMU as a herbicide the following phenomena would be expected. In soils high in organic matter or with deposits of vegetation or sawdust on the surface, the treatment will be somewhat less effective. Higher dosages may be required. More immediate effects of CMU on plants may be expected on sandy soils, but the chemical will be lost more readily than on heavier soils. Because equilibrium is established between adsorbed and aqueous phase, best results should be obtained under fairly moist but not excessively wet conditions.

Table II. Quantity of CMU Adsorbed

No.	Substance	CMU Ad- sorbed γ/G .
1	Asbestos	0
2	Cotton	0
3	Dicalite	0
4	Kaolin	0
5	Norite	8200
6	Sawdust	857
7	Straw	353

Table III. Correlation of Amount of Adsorption of CMU with Certain Soil Properties

Soil Property	Correlation Coefficient
Organic matter, %	0.999 ^a
	0.991
Clay, %	0.770 ^a
	0.209
Silt, %	0.358
pH	-0.497

^a Palouse silt loam was excluded from the calculations. This soil demonstrated unusual adsorptive properties not common to the other soils used in this study.

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Literature Cited

- (1) Assoc. Offic. Agr. Chemists, "Official Methods of Analysis," 7th edition, (3.39a) 1950. (3.3) 1950.
- (2) Bouyoucos, G. J., *J. Am. Soc. Agron.*, **22**, 747-51 (1930).
- (3) De Donder, Th., and Van Rysselberghe, P., "Thermodynamic Theory of Affinity," Stanford, Calif., Stanford University Press, 1936.
- (4) Kilmer, V. J., and Alexander, L. T., *Soil Sci.*, **68**, 15-24 (1949).
- (5) Loustalot, A. J., Muzik, T. J., and Cruzado, H. J., *Agr. Chemicals*, **8**, No. 11, 52 (1953).
- (6) Lowen, W. K., and Baker, H. M., *Anal. Chem.*, **24**, 1475-9 (1953).
- (7) Peech, Michael, U. S. Dept. Agr. *Circ.*, **757** (April 1947).
- (8) Snedecor, C. W., "Statistical Methods," Ames, Iowa, Iowa State College Press, 1940.
- (9) Tyner, E. H., *Proc. Soil Sci. Soc. Am.*, **4**, 106-13 (1939).

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ALFALFA CAROTENE

Stability of Carotene in Dehydrated Alfalfa Meal With Effect of Antioxidants, Oil, and Heat

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A study of the ability of certain chemicals to inhibit the oxidation of carotene in alfalfa meal during storage showed appreciable antioxidant activity in compounds related to aniline. The most promising was *N,N'*-diphenylhexamethylenediamine. Carotene retention during storage was influenced by the amount of oil which was used in applying the antioxidants to the meal. Applications of Wesson oil at the rate of 80 pounds per ton of meal were more effective than 16 pounds per ton in reducing oxidation. Heating the samples at 100° C. for an hour after spraying the meal with the oil resulted in a further increase in carotene retention.

STABILIZATION OF THE CAROTENE of dehydrated alfalfa meal by means of antioxidants has received much study in recent years. Kephart (4) proposed the use of *N,N'*-diphenyl-*p*-phenylenediamine, and this chemical has been approved by the U. S. Food and Drug Administration for use on alfalfa meal.

Table I. Antioxidant Activity of Aniline and Certain Derivatives

(0.2% antioxidant and Wesson oil at a rate of 16 pounds per ton)

Chemical	% Carotene Loss in 5 Months at 25° C.
None	60
Aniline	48
Monomethylaniline	40
Dimethylaniline	53
<i>N,N'</i> -Diphenylhexamethylenediamine	36
2,5-Di- <i>tert</i> -butylhydroquinone	35

The most extensive investigation has been reported by Thompson (7), who concluded that 2,5-di-*tert*-butylhydro-

quinone and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline were the most effective of the 54 chemicals tested.

Kephart (4) recommended that the antioxidant be applied by dissolving the chemical in a vegetable oil and spraying the solution on the meal. The oil is desirable also for controlling dustiness of the product, and is used for this purpose at rates of 7.5 to 25 pounds per ton of meal (8).

The data presented below show that certain derivatives of aniline possess considerable antioxidant potency, and that the effectiveness of a chemical can be enhanced by heavy oiling of the meal and by the application of heat.

Aniline Derivatives as Antioxidants

Alfalfa meal containing 25 mg. of carotene per 100 grams was sprayed in a rotary mixer with Wesson oil at a rate of 16 pounds per ton and with the various antioxidants at a level of 0.2% (2). The meals were stored in 4-ounce bottles at 25° C. and were analyzed for carotene at intervals by the method of Silker, Schrenk, and King (6). The aniline, monomethylaniline, and dimethylaniline used in the experiment were pur-

chased from various chemical supply houses. The *N,N'*-diphenylhexamethylenediamine was synthesized by reducing adipanilide with lithium aluminum hydride (7). The product had a melting point of 74° C.

The data are presented in Table I. The value of 2,5-di-*tert*-butylhydroquinone is included for comparison, because it was one of the better antioxidants studied by Thompson. All of the compounds had some antioxidant activity. Substitution in the amino group of aniline resulted in increased antioxidant potency, monomethylaniline having greater activity than either aniline or dimethylaniline. The activity of diphenylhexamethylenediamine was equal to that of 2,5-di-*tert*-butylhydroquinone. Thus, it may be possible to synthesize other derivatives which will have enhanced antioxidant activity, will possess the proper physical properties to facilitate application to the meal, and will have low toxicity.

Effects of Heat and Oil Level

Often it is difficult to duplicate industrial conditions on a laboratory scale. Oil frequently is applied commercially