

analyses are presented in Table V. The flame method would probably give slightly lower results for copper and manganese than the AOAC method, while iron is slightly higher. The results by the flame method are as precise as those by the AOAC method.

#### Acknowledgment

The authors wish to thank the Eli Lilly Corp. for financial sponsorship of this investigation and H. C. Fryer of the Kansas State College mathematics department for his consideration of the statistical results of this problem.

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**Table V. Comparison of Results on a Series of 10 Analyses on Same Sample**

	Copper, P.P.M.		Iron, P.P.M.		Manganese, P.P.M.	
	AOAC	Flame photometric (dry ash)	AOAC	Flame photometric (dry ash)	AOAC	Flame photometric (dry ash)
	31.5	37.5	43.0	47.5	37.7	35.0
	32.2	25.0	46.0	43.8	45.0	38.8
	37.8	29.5	37.0	40.0	39.0	38.0
	37.8	31.0	37.0	40.0	37.5	38.0
	39.0	31.2	38.0	45.5	39.0	37.0
	39.5	34.0	36.0	40.0	40.0	37.5
	40.2	32.2	40.0	36.2	39.0	35.0
	38.2	33.0	40.0	40.0	41.0	38.8
	42.0	37.0	42.0	43.8	41.0	37.5
	37.2	32.2	34.0	43.8	40.0	40.0
Mean	37.5	32.2	39.3	42.1	39.9	37.6
S.D.	3.21	3.60	3.62	3.36	2.14	1.60

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Received for review December 10, 1956.  
Accepted May 13, 1957. Contribution No. 551,  
Department of Chemistry. Portion of Ph.D.  
thesis, Kansas State College, Manhattan, Kan.

## HERBICIDE LEACHING

### Mobility of *N*-1-Naphthylphthalamic Acid (Alanap-1) in Soil

*N*-1-Naphthylphthalamic acid, a pre-emergence herbicide, shows moderate mobility in soil in spite of its very low water solubility. Although some mobility is desirable to assure even distribution of the chemical in the weed-producing soil layer, it should be controlled to protect semisensitive crops and to prolong residual herbicidal effect. Three ways of controlling the mobility of the herbicide have been found.

MOBILITY IN SOIL is an important factor in the performance of a pre-emergence herbicide. Some mobility in soil is desirable, to assure distribution throughout the weed-producing soil layer. It is advantageous, however, to limit the downward movement of the chemical in soil in heavy rainfall areas, as this prolongs the residual herbicidal effect and decreases chances of injuring deep-planted seeds of semisensitive crops.

The mobility of herbicides in soil varies greatly. Studies of the leaching characteristics of several herbicides were reported by Ogle and Warren (7). More

recently, the strong adsorption of 3-amino-1,2,4-triazole by soil particles was reported (4). In general, water-soluble herbicides tend to move readily with soil water, while most water-insoluble herbicides exhibit low mobility in soil. Although *N*-1-naphthylphthalamic acid has a very low water solubility, moderate mobility in soil was suspected from field performance data in 1952.

The Alanap herbicides (*N*-1-naphthylphthalamic acid derivatives) appear to give selective herbicidal action for two reasons: Some crops are only slightly susceptible—for example, most cucur-

bits—and crop seeds planted 1 inch or more below the soil surface are somewhat protected from chemicals applied to the surface; while weed seeds, which usually germinate in the top 1/4 inch of soil, are subjected to much higher concentrations of the chemical during the germination period. Injury to crops, such as cotton and beans, treated with *N*-1-naphthylphthalamic acid has varied from negligible to severe in field trials under different conditions. Differences in the amount of *N*-1-naphthylphthalamic acid leached to crop-seed depth in different tests could account for such variations.

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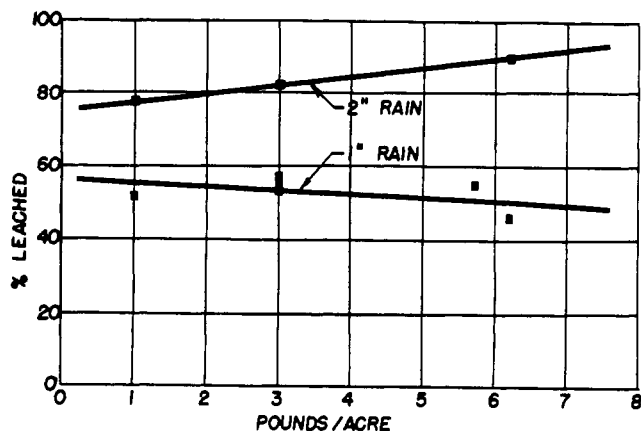


Figure 1. Effect of rate of application on leaching of *N*-1-naphthylphthalamic acid

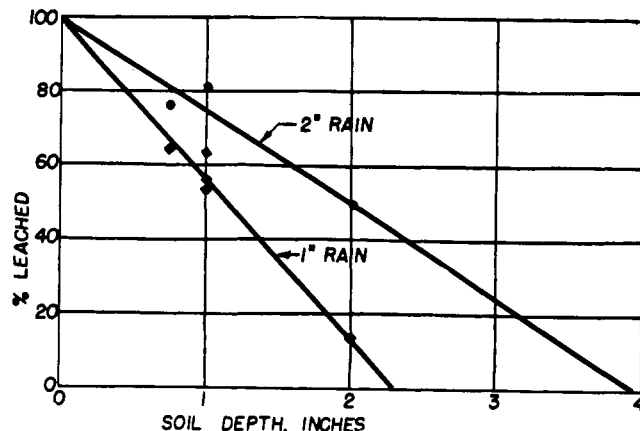


Figure 2. Effect of soil depth on leaching of *N*-1-naphthylphthalamic acid

A laboratory study of factors affecting the movement of the herbicide in soil was undertaken.

#### Test Methods

Sixty grams of a sandy loam (containing 7% moisture) is placed in a deep Büchner-type funnel with an inside diameter of 1<sup>7</sup>/<sub>8</sub> inches. The soil is packed to give a 1-inch layer by laying a thin sheet of rubber over the top of the funnel and applying vacuum for a few seconds. A known amount of the *N*-1-naphthylphthalamic acid formulation is applied to the surface. Fifty milliliters of water (equivalent to 1 inch of rainfall) is added and allowed to drain by gravity. The filtration is completed by applying vacuum to reduce the moisture content of the soil to approximate field capacity. The filtrate is analyzed chemically (3) to measure the amount of *N*-1-naphthylphthalamic acid removed.

#### Variables Affecting Leaching of *N*-1-Naphthylphthalamic Acid

In order to determine which variables were critical in obtaining consistent results with a given *N*-1-naphthylphthalamic acid formulation the following

experiments, which showed several important relationships, were run.

**Rate of Application.** The amount of *N*-1-naphthylphthalamic acid leached is proportional to the amount applied (the percentage leached is almost independent of rate applied) in the 1 to 8 pounds-per-acre range (Figure 1).

**Soil Depth.** The percentage of *N*-1-naphthylphthalamic acid leached varies inversely with soil depth. A plot of percentage leached vs. soil depth, with a constant amount of rain, gives an approximately straight line (Figure 2). Extrapolation to 0% leaching indicates that the maximum penetration of *N*-1-naphthylphthalamic acid under the conditions employed is roughly 2 inches per inch of rain.

**Amount and Time of Rainfall.** The time interval between application of the herbicide and the leaching operation does not seem to be critical. The amount of water applied is important. Equal successive increments of rain do not remove equal amounts of *N*-1-naphthylphthalamic acid, but rather remove approximately equal fractions of the amount remaining in the top inch of soil. Thus, 1 inch of rain removes 55% of the herbicide under standard conditions,

and a second inch of rain removes about half of the remaining 45%, or a total of 80% for 2 inches of rain (Figure 2).

**Soil Variables.** Variations in soil type cause large variations in the amount of leaching. Exact comparisons are difficult because of differences in moisture-holding capacity and density. There is some evidence that the degree to which the soil is packed and surface moisture content at the time of application of the herbicide may affect the amount of leaching. A sandy loam soil containing 7% moisture was the standard used in all formulation studies. In the cases tested, the formulation additives, which improved performance on the standard soil, were also effective on the other soil types.

On the basis of the above work the following conditions were selected as standard: soil, a sandy loam, pH 5.6; soil depth, 1 inch; herbicide application, *N*-1-naphthylphthalamic acid at 5 pounds per acre; amount of water, equivalent to 1 inch of rain.

#### Ways of Decreasing Mobility of *N*-1-Naphthylphthalamic Acid

Formulation studies with *N*-1-naphthylphthalamic acid indicated feasible variations in the amount of wetting agent, and that particle size had relatively little effect on the amount of leaching.

Three ways of effecting major changes in the soil mobility of Alanap herbicides have been found (2). The first way is by use of a derivative such as an ester or the imide instead of the free acid or salt. These nonionizing forms exhibit very low soil mobility, but cost and performance considerations limit the usefulness of this approach. The fact that these nonionizing derivatives are immobile, while the soluble salts and insoluble acid both are mobile in soil, led to a consideration of the mechanism of leaching.

When *N*-1-naphthylphthalamic acid dissociates ( $HA \rightleftharpoons H^+ + A^-$ ) the free phthalamate ions would be expected to move readily with soil water, as do

Table I. Formulation with Electrolytes

(*N*-1-Naphthylphthalamic acid at 4 pounds per acre in 500 gallons of spray solution containing electrolyte)

Electrolyte	Lb./Acre	<i>N</i> -1-Naphthylphthalamic Acid Leached, %	I.F. <sup>a</sup>
None	...	41-56 <sup>b</sup>	1.0
H <sub>2</sub> SO <sub>4</sub> (3%)	120	5	10.0
H <sub>2</sub> SO <sub>4</sub> (1%)	40	10	5.0
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (3%)	120	58	0.8
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> nH <sub>2</sub> O (3%)	120	6	8.3
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> nH <sub>2</sub> O (1%)	40	24	2.1
FeCl <sub>3</sub> (3%)	120	12	4.2
BaCl <sub>2</sub> (3%)	120	32	1.6
CaCl <sub>2</sub> (3%)	120	56	0.9

<sup>a</sup> Improvement factor =  $\frac{\% \text{ leached from } N\text{-1-naphthylphthalamic acid std.}}{\% \text{ leached from experimental formulation}}$

<sup>b</sup> Average, 50%.

most monovalent anions. Organic acids would probably dissociate extensively even in slightly acidic soils as the cation exchange substances of the soil have a high affinity for hydrogen ions which displace sodium, ammonium, calcium, and most other cations from the soil micelles. Any removal of protons favors further ionization and dissociation of the acid. This theory emphasizes the role of the soil as a reactive system rather than an inert medium.

A second effective way of controlling the herbicide leaching is to mix it with relatively large amounts of a substance which furnishes cations for which the soil has a high affinity. The cation capacity of the soil surface around each herbicide particle is thus satisfied by cations not easily displaced by protons, and the *N*-1-naphthylphthalamic acid dissociation equilibrium is not upset by proton removal.

When sulfuric acid, aluminum sulfate, or ferric chloride is added to the spray mixture, the tendency of the *N*-1-naphthylphthalamic acid to leach is reduced (Table I). The sulfuric acid provides enough hydrogen ions to react with the soil as discussed above. While the salts hydrolyze to give acid solutions, this cannot fully explain their effectiveness, as ammonium sulfate, which is also acidic in water, is not effective in retarding leaching. The authors believe the aluminum and ferric ions are effective because they, like hydrogen ions, are tightly bound by the soil. The amount of calcium chloride used had little or no effect, which is logical as calcium ions are displaced from soil micelles by hydrogen ions, unless a very large excess of calcium ion is present.

Some data indicate that less additive would give equivalent results if the herbicide were applied with less water. Similar effects have been obtained on three other soil types. Good control of leaching can be obtained by this method, and biological tests of such formulations have shown no loss of herbicidal activity.

A representative formulation containing 1% of *N*-1-naphthylphthalamic acid, 33% of sodium bisulfate, and 66% of mineral diluent was tested for leaching tendency against a similar formulation containing no bisulfate. These formulations were applied to the soil as dry powders. Alanap-1 (*N*-1-naphthylphthalamic acid) was included in the test—applied as an aqueous suspension. Results are summarized in Table II. The formulation with sodium bisulfate reduced the amount leached to 5% in comparison with the standard formulation, which showed 50% leached. The decrease in soil mobility was not accompanied by reduced herbicidal activity.

A practical use of this type of formulation of *N*-1-naphthylphthalamic acid

with an electrolyte is for application to lawns to give long residual action against germinating crab grass seeds.

The third effective way to control the mobility of *N*-1-naphthylphthalamic acid in soil is by formulating with water-insoluble organic acids—e.g., stearic acid. The water-soluble organic acids—e.g., acetic acid—are ineffective in similar amounts. The function of these additives is not entirely clear but two factors were considered:

The effect may be purely physical, a coating of waxy solid protecting the *N*-1-naphthylphthalamic acid, or the insoluble acid may work because it serves as a source of hydrogen ions.

If the first explanation is correct, non-acidic substances of suitable physical properties should be effective also. Small amounts of paraffinic wax (5 to 15%) appear to help, but the effect is small and formulation difficulties with such mixtures have prevented a fair comparison. Waxy substances containing polar groups, such as a carboxyl group, give better formulation charac-

teristics. In this case, waxy esters or alcohols might also be effective. Table II shows data from an experiment using cetyl alcohol and carnauba wax with the *N*-1-naphthylphthalamic acid (1 to 1 ratio).

The alcohol had only a small effect on leaching. Carnauba wax is mainly a waxy ester but contains some free fatty acid and has an acid number about one tenth that of stearic acid. It was more efficient than cetyl alcohol in decreasing leaching of the herbicide, but was much less effective than stearic acid, indicating that the hydrogen ion is important. However, as small amounts of weak organic acids of high equivalent weight are more effective than equivalent amounts of sulfuric acid, the effect does not seem entirely due to the availability of the hydrogen ion. Nor is it simply a matter of the water insolubility of the additive, because when the strongly acidic hydrogen form of an insoluble cation exchange resin (Amberlite IR-120) was ground with *N*-1-naphthylphthalamic acid (1 to 1) the resultant formulation leached as badly as the standard. In this formulation, the resin and *N*-1-naphthylphthalamic acid did not appear to be mixed within individual particles.

Formulations with stearic acid have been prepared in various ways: by coprecipitating the acids from solutions of the sodium salts; by dissolving the stearic acid in an *N*-1-naphthylphthalamic solvent slurry and evaporating the solvent; by melting the stearic acid, stirring in the *N*-1-naphthylphthalamic acid, and cooling; and by simple mechanical mixture. Similar formulations have been made using rosin acids. In all cases, the mixtures were formulated with surfactants, cooled, and ground, giving wetttable powders. Incorporating the additive by mechanical mixing was ineffective; by coprecipitation, it was more effective; and by comelting and solvent techniques, the best control of leaching was realized. The data in Table III are representative results obtained with the standard soil showing a reduction in per cent leached when *N*-1-naphthylphthalamic acid is formulated with insoluble organic acids. Generally, similar results have been noted in work on other soil types.

A representative experimental formulation consisting of 50% of *N*-1-naphthylphthalamic acid, 20% of stearic acid, 25% of talc, and 5% of surfactants was tested. This type of formulation has given batches having desirable soil mobility characteristics (improvement factor of 3 to 10) and unimpaired herbicidal effectiveness. The effects of soil depth and amount of rainfall on the leaching of this formulation are shown in Figure 3. The effect of soil depth is different in this case than with *N*-1-naphthylphthalamic acid.

The leaching tendencies of *N*-1-

**Table II. Formulation with Sodium Bisulfate and Waxy Substance**

Formulation	Leached, %	I.F. <sup>a</sup>
SODIUM BISULFATE		
<i>N</i> -1-Naphthylphthalamic acid	50	1.0
1% <i>N</i> -1-naphthylphthalamic acid + 99% mineral diluent	67	0.75
1% <i>N</i> -1-naphthylphthalamic acid + 33% NaHSO <sub>4</sub> + 66% mineral diluent	5.2	9.6
WAXY SUBSTANCES		
<i>N</i> -1-Naphthylphthalamic acid std.	50	1.0
<i>N</i> -1-Naphthylphthalamic acid + cetyl alcohol 1:1	39	1.3
<i>N</i> -1-Naphthylphthalamic acid + carnauba wax 1:1	20	2.5
<i>N</i> -1-Naphthylphthalamic acid + stearic acid 1:1	10	5.0

<sup>a</sup> See footnote a, Table I.

**Table III. Formulation with Insoluble Acids**

(*N*-1-Naphthylphthalamic acid + insoluble acid (1:1) formulations)

Type	Leached, %	I.F. <sup>a</sup>
<i>N</i> -1-Naphthylphthalamic acid standard	50-60 <sup>b</sup>	1.0
Rosin K, coprecipitation method	13	4.2
Stearic acid, coprecipitation method	25	2.2
Stearic acid, solvent method	9	6.1

<sup>a</sup> See footnote a, Table I.

<sup>b</sup> Average, 55%.

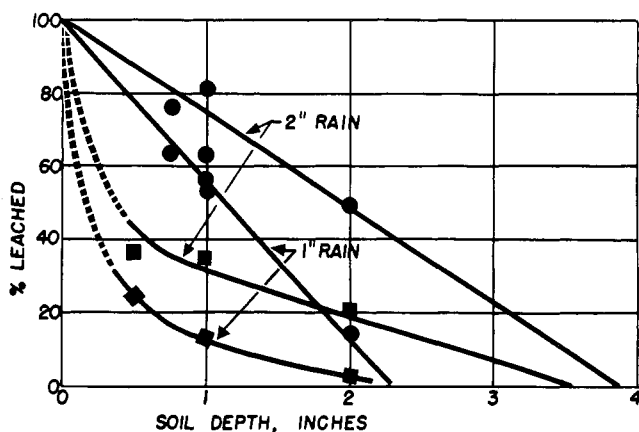


Figure 3. Effect of soil depth on leaching

● *N*-1-naphthylphthalamic acid  
 ■ Experimental form with stearic acid

naphthylphthalamic acid and this experimental formulation have been compared on three soil types: the standard soil, a silt soil from Mississippi, and a black loam from Illinois. Under the standard test conditions, the experimental formulation with stearic acid retarded leaching on the soils tested (Table IV).

The incorporation of water-insoluble acids to control the soil mobility of *N*-1-naphthylphthalamic acid is a more versatile technique than the electrolyte method. Wettable powder and granular type formulations are being tested.

The authors believe that the effectiveness of stearic and similar insoluble organic acids, in decreasing the mobility of *N*-1-naphthylphthalamic acid in soil,

is due to the following factors: The waxy additive tends to coat and protect the particles of herbicide from contact with the soil and water; the additive furnishes hydrogen ions, which react with the soil and decrease its tendency to ionize the herbicide; and one equiv-

alent of a weak acid (such as stearic) is as effective as a manifold excess of a much stronger acid (such as sulfuric). This is explained by the fact that when the organic acid additive and the herbicide are properly blended, each particle carries its own antileaching agent, the hydrogen-donating activity of the additive is confined to soil in the immediate vicinity of each particle. In the case of water-soluble acids the effect is dissipated over the entire soil surface.

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Received for review October 20, 1956. Accepted April 4, 1957. Division of Agricultural and Food Chemistry, Pesticides Subdivision, 130th Meeting, ACS, Atlantic City, N. J., September 1956.

Table IV. Effect of Soil Variations

Soil	<i>N</i> -1-Naphthylphthalamic Acid, % Leached	Experimental Formulation	
		Leached, %	I.F. <sup>a</sup>
Standard sandy loam	56	14	4.0
Mississippi silt	68	24	2.8
Illinois black loam	55	20	2.8

<sup>a</sup> See footnote a, Table I.

## REPELLENT ANALYSIS

### Separation and Differentiation of Mixtures of 2,3,4,5-Bis( $\Delta^2$ -butenylene)tetrahydrofurfural, Its Alcohol, and Its Acid, by Paper Chromatography

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2,3,4,5-Bis( $\Delta^2$ -butenylene)tetrahydrofurfural has been proposed for use as a fly repellent. A method whereby it and its alcohol and acid derivatives may be readily separated by paper chromatography is given.

A PAPER CHROMATOGRAPHIC PROCEDURE for the separation and identification of 2,3,4,5-bis( $\Delta^2$ -butenylene)tetrahydrofurfural, its alcohol, and its acid is outlined. The aldehyde, also known as R-11, has been proposed as a fly repellent for dairy cattle.

#### Apparatus

Tank and accessories, as described by Mitchell (2-4).

Filter paper, Whatman No. 1, 8 × 8-inch sheets.

Sprayer, for application of immobile solvent and chromogenic agents. (A suitable glass sprayer is supplied by University Apparatus Co., Berkeley, Calif., which also supplies glass troughs and clips.)

#### Reagents

1. Immobile Solvent. Dimethyl formamide (Matheson, Coleman, and Bell, Inc., East Rutherford, N. J.), 20% (v./v.) solution in ethyl ether, ACS grade.

2. Mobile Solvent. Mixed octanes,

commercial grade (Phillips Petroleum Co., Bartlesville, Okla.).

3. Chromogenic Agents. (a) Dissolve 1 gram of potassium periodate in 100 ml. of water. (b) Dissolve 1 gram of potassium permanganate and 2 grams of sodium carbonate in 100 ml. of water. Immediately prior to spraying, mix four parts of (a) with one part (b) (7).

4. Standards. Dissolve 0.2 gram of each substance, and a mixture of 0.2 gram each of all three substances, in 10-ml. volumes of ethyl acetate. Dilute 0.5 ml. of each of the four solutions to 10-