

to 71%. Under the same conditions, kaolinitic and montmorillonitic clays, fuller's earth, and phosphate by-product with bulk densities in the range 23 to 40 pounds per cubic foot effected reductions in the range 29 to 41%. Calcium carbonate, pyrophyllitic clay, and spent fuller's earth with bulk densities in the range 42 to 55 pounds per cubic foot, effected reductions of less than 17%. A 1% addition of diatomaceous earth with bulk density of 10 pounds per cubic foot was more effective than 3% additions of either kaolinitic clay or spent fuller's earth with bulk densities of 40 and 55 pounds per cubic foot, respectively.

Caking tendency of uncoated granular 12-12-12 fertilizer decreased with extension of the curing period from 1 to 8 days. Percentage reductions in crushing strength of cake attributable to presence of coating agents were largely independent of the curing time. Reducing the particle-size range of fertilizer from 10-20 mesh to 20-35 mesh increased the caking

tendency of fertilizer 18% but did not significantly alter the effect of 2% additions of diatomaceous earth. Caking tests conducted with regular-shaped and crushed irregular-shaped granules of 8-16-16 fertilizer indicated that coating agents were substantially more effective in reducing the caking tendency of fertilizer when used with the regular-shaped granules. In general, the study showed that a number of finely divided materials of low bulk density currently marketed may be used as coating agents to effect significant reductions in caking tendency of granular fertilizers.

Acknowledgment

The authors wish to thank the producers who furnished samples of their materials for these tests and to express their appreciation to John B. Breen for general laboratory assistance and to G. W. Wieczorek for particle-size evaluations of coating agents.

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UREA-FORMALDEHYDE FERTILIZERS

Solubility Relationships and Nitrification Characteristics of Urea-Form

K. G. CLARK, J. Y. YEE,
V. L. GADDY, and F. O. LUNDSTROM
Fertilizer and Agricultural Lime
Section, Soil and Water Conservation
Research Branch,
Agricultural Research Service,
U. S. Department of Agriculture,
Beltsville, Md.

Solubility relationships and nitrification characteristics are reported for urea-formaldehyde reaction products ranging from 0.75 to 1.4 in mole ratio of urea to formaldehyde. Although possible suitability of such materials for fertilizer use is indicated by $U/F > 1$, increases in this ratio are not necessarily directly related to improved solubility and nitrification characteristics. The primary components of the neutral permanganate activity, the solubility pattern, and the activity index recently adopted by the Association of Official Agricultural Chemists, were found to be highly correlated with the degree of nitrification observed in a 3-week incubation period. Increase in nitrification between 3- and 15-week incubation periods was more highly correlated with the secondary components of the solubility pattern and activity index than with that of the permanganate procedure. In consequence, the solubility pattern procedure and the recently adopted activity index, $AI \leq 40$, are considered more reliable than neutral permanganate activity in characterizing the suitability of urea-formaldehyde materials for fertilizer use.

THE GENERIC TERM "UREA-FORM" has been applied to urea-formaldehyde fertilizer materials. Such products have been described as mixtures of polymethyleneureas (β , δ) which exhibit urea-formaldehyde mole ratios greater than 1, $U/F > 1$, nitrogen contents in excess of 37%, low solubilities in water and organic solvents, and lower rates of nitrification in soil media than the more soluble forms of chemical nitrogen fertilizers. The present paper reports the composition and solubility and nitrifi-

cation characteristics of a wide variety of urea-formaldehyde reaction products in relation to their suitability for fertilizer use.

Urea-Formaldehyde Mole Ratio

The fact that urea and formaldehyde react to form products with $U/F > 1$ requires at least some of the urea residues to be present as branched- or straight-chain methylene linkage-type polymers

in which $2 \leq U/F = \frac{n+1}{n} \leq 1$, as shown in Figure 1. For large values of n , $U/F \approx 1$, whereas for $n = 1$, $U/F = 2$ and the product is soluble methylenediurea.

Any degree of cross linkage between the urea residues in the polymer results in a decrease in the U/F mole ratio to the range $1/2 \leq U/F = \frac{m+1}{2m} = \frac{m+n+2}{2m+n+1} \leq 1$. The highly cross-

Table I. Properties of Some Urea-Formaldehyde Reaction Products

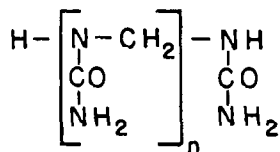
Sample No.	Analysis		Nitrification in Soil, 30° C.			Index, 100 X (15 wk.-3 wk.) / (100-3 wk.), %	Neutral Permanganate Solubility (2)			Solubility Pattern, 30° C. (6)			AOAC Activity (7)			
	Total N, %	Urea N, %	Urea/Formaldehyde, mole ratio	Incubation Period, Weeks			Increase ^a , 3 to 15 wk.	WIN, % of total N	PIN, % of total N	Activity, 100 X (WIN-PIN) / (WIN), %	Primary solubility, A, % of total N	Secondary solubility, B, % of total N	Index, 100 X (B ₂) / (100-A), %	HWIN, % total N	Index, Al, 100 X (WIN-HWIN) / (WIN), %	
				3	9											15
1	20.38	0.06	28.88	0.75	8.3	23.7	28.3	20.0	1.8	97.7	36.8	1.3	33.4	57.3		
2	20.56	0	29.02	0.76	1.4	4.1	3.4	2.7 ^b	100.0	73.4	2.3	0	98.6	1.5		
3	21.16	0.09	28.18	0.80	3.0	8.8	10.0	7.0	54.4	42.9	10.7	0.2	77.4	18.7		
4	20.50	0.11	25.36	0.86	7.1	17.0	21.1	14.0	78.3	75.3	37.3	2.6	51.2	34.6		
5	19.53	0.04	21.59	0.97	4.1	2.8	4.4	0.8 ^c	100.0	58.8	2.8	0.8	92.0	8.0		
6	23.65	4.0	7.4	12.2	8.2	83.2	58.4	22.2	2.7	58.0	30.3		
7	23.45	...	25.09	1.00	0	1.2	3.0	3.0	74.4	25.2	0	0	95.4	4.2		
8	20.69	3.17	13.26	1.42	27.6	32.9	38.5	11.1	15.3	34.3	31.8	7.2	56.5	26.1		
9	36.68	1.35	33.77	1.12	16.4	21.2	17.3	4.8 ^b	67.3	97.9	37.3	2.6	45.3	32.7		
10	39.38	21.8	33.9	39.9	18.1	64.8	96.2	32.2	3.0	38.6	40.4		
11	38.11	0.41	34.56	1.17	15.1	46.3	53.9	38.8	82.0	98.3	31.5	20.2	22.8	72.3		
12	36.95	0.36	33.32	1.19	1.8	15.5	22.4	20.6	95.2	90.1	5.6	5.7	63.1	33.7		
13	37.09	2.40	31.17	1.19	16.8	30.4	35.4	18.6	80.4	90.8	27.8	9.2	40.9	49.1		
14	36.04	1.19	30.90	1.21	12.4	22.1	26.5	14.1	68.1	98.6	33.2	4.2	41.0	39.2		
15	37.98	0.31	33.40	1.21	12.6	54.4	55.5	42.9	82.1	97.9	32.2	20.1	21.8	73.4		
16	37.50	3.15	30.21	1.22	20.8	37.1	47.4	26.6	76.1	90.5	33.3	14.5	30.6	59.5		
17	38.15	4.27	29.24	1.24	22.6	30.7	32.4	9.8	52.9	87.6	48.6	4.9	33.2	37.3		
18	37.27	1.40	30.75	1.25	13.7	25.5	27.2	13.5	75.7	75.6	25.1	3.2	59.6	21.3		
19	37.71	1.77	30.76	1.25	9.4	20.9	31.7	22.3	84.5	74.7	19.8	4.1	59.5	29.5		
20	36.81	0.26	31.25	1.25	2.7	43.5	51.4	48.7	77.2	98.0	37.9	21.7	18.6	76.0		
21	36.96	0.31	31.26	1.26	7.0	53.0	57.4	50.4	79.1	97.9	37.6	23.3	17.8	77.5		
22	39.04	4.05	29.06	1.29	15.7	31.6	47.1	31.4	70.4	75.8	30.2	7.9	43.0	38.9		
23	38.95	2.65	30.08	1.29	28.7	59.3	69.0	40.3	62.9	100.0	46.6	21.6	14.3	77.2		
24	38.55	0	31.83	1.30	0.4	44.9	66.0	65.6	94.6	97.6	6.7	21.4	30.4	67.9		
25	39.28	2.16	30.34	1.31	22.2	39.9	49.9	27.7	71.5	82.7	30.9	9.6	39.0	45.5		
26	38.50	0.44	31.10	1.31	6.8	38.6	59.9	53.1	88.4	96.8	14.3	18.7	11.6	72.6		
27	39.12	3.07	29.49	1.31	35.4	68.5	78.4	43.0	57.6	100.0	55.3	22.1	8.6	85.1		
28	39.81	4.28	28.73	1.32	33.0	44.7	55.7	22.7	60.3	93.3	44.0	11.4	25.9	52.0		
29	39.26	4.58	27.91	1.33	19.7	32.1	46.3	26.6	63.3	79.0	39.0	8.7	33.6	47.0		
30	39.06	4.37	28.04	1.33	23.4	35.7	44.6	21.2	59.8	86.5	42.8	9.4	30.9	48.3		
31	37.59	5.57	25.80	1.33	34.2	48.8	60.1	28.2	68.8	84.6	38.7	9.4	36.6	46.8		
32	39.44	5.70	26.82	1.35	23.7	42.1	49.0	25.3	62.8	73.8	39.3	7.5	39.8	36.6		
33	37.95	4.29	26.79	1.35	29.7	47.3	61.8	32.1	58.2	89.3	49.0	11.2	25.7	55.8		
34	38.63	5.48	25.89	1.37	35.2	48.4	53.3	18.5	59.5	77.7	44.4	8.1	34.9	41.4		
35	39.69	4.91	27.19	1.37	36.1	52.8	59.4	24.8	52.4	93.1	54.2	14.5	20.9	60.2		

^a Increase between 3 and 15 weeks except as noted.^b Maximum nitrification observed at 9 weeks.^c Maximum nitrification observed at 13 weeks.

WIN. Water-insoluble nitrogen.

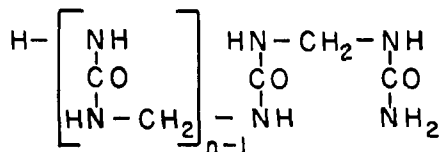
PIN. Neutral permanganate-insoluble nitrogen.

HWIN. Hot water-insoluble nitrogen.



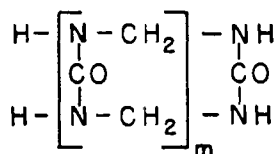
$$2 \geq U/F = \frac{n+1}{n} \geq 1$$

Parallel or Branched Chain Polymer



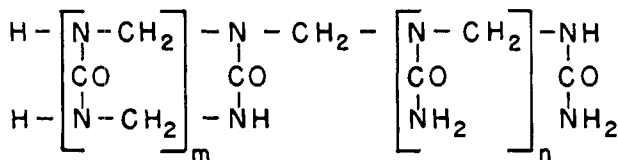
$$2 \geq U/F = \frac{n+1}{n} \geq 1$$

Straight Chain Polymer



$$\frac{1}{2} \leq U/F = \frac{m+1}{2m} \leq 1$$

Cross-Linked Polymer



$$\frac{1}{2} \leq U/F = \frac{m+n+2}{2m+n+1} \leq 1$$

Hybrid Straight or Branched Chain and Cross-Linked Polymer

Figure 1. Typical urea-formaldehyde mole ratio relationships

linked structure assigned by Marvel and associates (12) to urea-formaldehyde resins and involving methylene linkages between cyclic trimethylenetriurea molecules with $U/F \approx 2/3$ is equivalent to $m = 3$ in the absence of chain linkages between urea residues. From these considerations it is apparent that materials with $U/F > 1$ may consist either of $(n+1)/n$ type materials alone or of both the chain and cross-linked types.

The relation between the $U/F \approx 1$ and $U/F \geq 1$ types of polymers in a mixture is

$$(U/F)_{\text{obsd.}} = \frac{1}{\frac{x}{r} + \frac{1-x}{t}}$$

where x is the fraction of the urea combined in the chain-type polymer, r the weighted average U/F value for this type, and t that for the cross-linked type. For $r = (U/F)_{\text{obsd.}}$, all of the urea must be present as straight- or branched-chain methyleneurea polymers. However, for $r > (U/F)_{\text{obsd.}}$, it may be shown the x is a minimum for the maximum values of t and r , or 1 and 2 respectively. The expression for the minimum value of x then becomes

$$x_{\text{min.}} = \frac{r}{r-t} \left[\frac{(U/F)_{\text{obsd.}} - t}{(U/F)_{\text{obsd.}}} \right] = \frac{2}{2} \left[\frac{(U/F)_{\text{obsd.}} - 1}{(U/F)_{\text{obsd.}}} \right]$$

This relation between the observed U/F value of a product and the minimum percentage of the combined urea present as chain-type polymers is represented graphically in Figure 2. For an observed U/F value of 1.25 not less than 40% of the combined urea must be present as $(n+1)/n$ type compounds, and as much as 100% may be in this form. In the case of products of low solubility containing little or no soluble methylenediurea $r < 2$ and the portion of the urea present as $(n+1)/n$ type compounds exceeds the indicated minimum. Thus, the suitability of materials with $U/F > 1$ may well depend not only on the U/F value and the relative proportions of the chain and cross-linked types of polymers present, but also on the distribution of the individual polymers within the $(n+1)/n$ group and hence on the solubility characteristics of the material.

Solubility and Nitrification

The work of Rubins and Bear (14) indicated that solubility in neutral permanganate as determined by the official method of the Association of Official Agricultural Chemists (1) was not reliable for all types of urea-formaldehyde products in relation to nitrification and to vegetative response. Clark and Gaddy (4) found that the

official AOAC neutral and alkaline permanganate procedures failed properly to evaluate the water-insoluble nitrogen content of many mixed fertilizers in comparison to observed nitrification in soil media. Yee and Love (17) reported that solubility in water and rate of nitrification of similarly prepared urea-formaldehyde reaction products with $U/F > 1$ increased with an increase in the U/F ratio in line with the required increase in the minimum fraction of chain-type compounds. Later, Clark, Yee, Love, and Boyd (6) reported correlations between the nitrification characteristics of urea-formaldehyde products prepared by differing processes and the solubility pattern, A/B_x , of the nitrogen content determined by two successive 24-hour water digestions of a 1-gram sample at 30° C. Subsequently, Morgan and Kralovec (13) and Kralovec and Morgan (9) described a procedure for evaluating the suitability of urea-formaldehyde materials for fertilizer use based on differential solubility of the nitrogen in water at 25° C. and in a phosphate-buffered solution of pH 7.5 at 99° to 100° C. More recently and after collaborative study (7), the AOAC (15) adopted as first action the Morgan-Kralovec "activity index" method for determining the quality of urea-formaldehyde compounds. Thereafter, the Association of American Fertilizer Control Officials adopted as tentative (7) a minimum AI value of 40 for urea-formaldehyde fertilizer materials.

Experimental

A total of 35 urea-formaldehyde reaction products known to vary widely in formulation and in method of preparation were selected for determination of their nitrogen and formaldehyde contents, neutral permanganate activities, solubility patterns, activity indexes, and nitrification characteristics in soil media. Where necessary, the samples were

Figure 2. Relation between U/F mole ratio and minimum portion of urea combined as $U/F > 1$

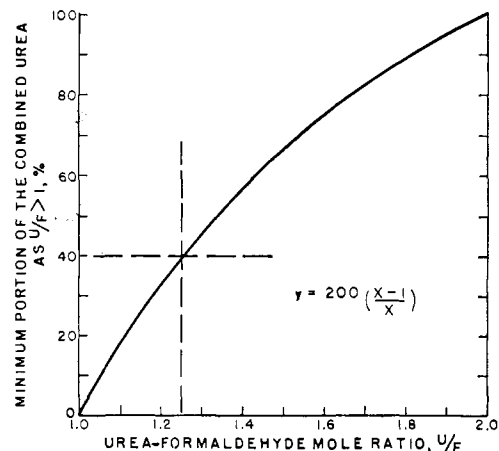


Table II. Comparable Nitrification and Solubility Factors

Factor	Nitrification	Neutral Permanganate Solubility	Solubility Pattern	Activity
Primary				
Secondary	N_3^a	WIN ^b	A^c	WIN ^b
A	N_{15}^d	PIN ^e	$A + B_z$	HWIN ^f
B	$(N_{15} - N_3)$	(WIN-PIN)	B_z^g	(WIN-HWIN)
Index	$\frac{100(N_{15} - N_3)}{100 - N_3}$	$\frac{100(\text{WIN-PIN})}{\text{WIN}}$	$\frac{100 B_z}{100 - A}$	$\frac{100(\text{WIN-HWIN})}{\text{WIN}}$

^a Degree of nitrification in 3 weeks, 30° C.
^b AOAC water-insoluble nitrogen.
^c Degree of nitrogen solubility, 1-g. sample in 400 ml. of water, 30° C., 24 hr.
^d Degree of nitrification in 15 weeks, 30° C.
^e AOAC neutral permanganate-insoluble nitrogen.
^f Hot phosphate buffer solution-insoluble nitrogen, pH 7.5, 100° C.
^g 400 ml. insoluble 2000 ml. water-soluble nitrogen, 30° C., 24 hr.

crushed to pass a 20-mesh (0.833-mm.) sieve and thoroughly mixed prior to sampling for analysis, nitrification studies or solubility determinations.

Analytical Methods Total nitrogen was determined either by the Kjeldahl method or by a modification of the Marcali-Rieman procedure (11) for the Kjeldahl determination of nitrogen without distillation. Uncombined or free urea nitrogen was determined by the method of Yee and Davis (16), and formaldehyde by a modification of the Levenson method (10).

Water-insoluble nitrogen and neutral permanganate-insoluble nitrogen were determined by AOAC procedures (2). The primary and secondary nitrogen solubilities, A and B_z, were determined by the method of Clark, Yee, Love, and Boyd (6). Hot water-insoluble nitrogen was determined by the Morgan-Kralovec phosphate buffer solution procedure (7, 9, 13) recently adopted first action by the AOAC (15). All analyses were conducted in duplicate.

Nitrification Studies The following procedure was used in determining the degree of nitrification after 3-, 6-, 9-, 12-, and 15-week incubation periods. A 20-mg. nitrogen equivalent of a sample was mixed with 100 grams of minus 20-mesh air-dried Morgnac silt loam soil in a 500-ml. Erlenmeyer flask and the leveled mixture overlain with an additional 10 grams of soil. Before use, the pH of the soil was adjusted to the range 6.9 to 7.1 by addition of calcium carbonate. The moisture content of the mixture was adjusted to the moisture equivalent of the soil (3), approximately 20%, the flask lightly stoppered with a cotton plug, and the mixture incubated at 30° C. for the desired periods with weekly replacement of any water lost by evaporation. At the end of an incubation period, the nitrate content of the mixture was extracted and determined photometrically by the phenoldisulfonic acid procedure (8). In general, triplicate incubations were employed with single

determinations of the nitrate content of each replicate. The result was corrected for the nitrate found in a similarly incubated and extracted soil blank, and the corrected result was expressed in terms of the percentage of the added nitrogen which had been converted to nitrate form.

It was not possible to conduct the nitrification studies on all samples simultaneously. Ammonium sulfate controls were included in each series of studies to indicate whether the observed nitrifications of the samples were being limited by inadequate nitrifying capacity of the soil. The degree of nitrification of ammonium sulfate ranged between 85 and 95% for the 3-week incubation periods and greatly exceeded the degrees observed for the urea-formaldehyde samples at all other periods. It was concluded, therefore, that nitrifying capacity was not a limiting factor in any series.

Discussion of Results

The analytical results, including the observed degrees of nitrification at the end of the 3-, 9-, and 15-week incubation periods, and the several indexes calculated therefrom are presented in Table I. The total nitrogen, urea nitrogen, and formaldehyde equivalent are reported on the weight per cent basis, whereas for convenience in making comparisons the degree of nitrification, water-insoluble nitrogen (WIN), neutral permanganate-insoluble nitrogen (PIN), primary and secondary nitrogen solubilities A and B_z, and the hot water-insoluble nitrogen (HWIN) are expressed as per cent of the total nitrogen content of the sample.

The difference between the total nitrogen (column 2) and the uncombined urea nitrogen (column 3) was taken as urea nitrogen combined with formaldehyde and used in calculation of the U/F mole ratio (column 5).

All three solubility procedures involve primary and secondary relationships.

Both the neutral permanganate activity and the activity index procedures combine these factors into a single index indicating the percentage of the nitrogen insoluble in the primary procedure which was found to be soluble by the secondary procedure. In contrast, the solubility pattern, A/B_z, directly indicates both the primary and secondary nitrogen solubilities and presumably the more and less readily nitrifiable components of the sample, respectively. However, this pattern may be readily converted to a comparable index (column 16), $\frac{100 B_z}{100 - A}$, which like the other indexes tends to obscure the primary factor.

Likewise a comparable nitrification index (column 10), $\frac{100(N_{15} - N_3)}{100 - N_3}$,

may be formulated from the nitrification data by taking the degrees of nitrification in 3 and 15 weeks as the primary and secondary factors, respectively. Comparable terms are then available for comparing individual factors and indexes among the four evaluation procedures, as shown in Table II. The solubility procedures employed are empirical and of value for laboratory evaluation of urea-formaldehyde reaction products only if they can be correlated with vegetative response or with nitrification behavior. Nitrification behavior generally is accepted as a valid measure of probable vegetative response to other than the ammonium and nitrate forms of fertilizer nitrogen. Consequently, statistical analysis was used to determine the degree of correlation between nitrification behavior and the several primary, secondary, and index factors.

Table III. Correlation Coefficients between Primary Factors^a

Factor	Water-Insoluble Nitrogen, WIN	Primary Solubility, A
Nitrification in 3 weeks	-0.86	+0.80
Water-insoluble nitrogen	...	-0.94

^a All correlations significant at 1% level.

Primary Solubility Factors

Table III gives the correlation coefficients among the several primary factors. All correlations exceeded the requirement for significance at the 1% level. Water-insoluble nitrogen was found to be somewhat more highly correlated with nitrification in 3 weeks, N₃, than the primary solubility, A. The data for the better correlation are plotted in the scatter diagram, Figure 3, which also includes the regression line and equation for N₃ as the independent variable. Assuming that the degree of nitrification in 3 weeks equals or exceeds

15%, this diagram indicates that in general the water-insoluble nitrogen is less than 75% of the total. A scatter diagram between N_3 and A shows $A \approx 25$ for $N_3 \approx 15$.

Secondary Solubility Factors

Correlations between secondary factors are indicated in Tables IV and V. Although the correlations among the Type A and Type B factors are highly significant in all cases, it is apparent that the neutral permanganate solubility is the least reliable of the three procedures for evaluation of either the total degree of nitrification in 15 weeks, N_{15} , or the increase in nitrification between 3 and 15 weeks, $N_{15} - N_3$. The hot water-insoluble nitrogen content appears to be a better measure of total nitrification than the solubility pattern procedure, but the reverse is the case for the increase in nitrification between 3 and 15 weeks.

Figure 4 is the scatter diagram for the correlation between the water-insoluble hot water-soluble nitrogen, WIN-HWIN, and the increase in nitrification between 3 and 15 weeks, $N_{15} - N_3$. Assuming in this case that the increase in nitrification is not less than 25% of the total nitrogen indicates that $WIN-HWIN \approx 30$. Scatter diagrams between $N_{15} - N_3$ and B_x or WIN-PIN show that $B_x \approx 10$ and WIN-PIN ≈ 60 for $N_{15} - N_3 \approx 25$.

Indexes

The several correlations among the index factors are presented in Table VI. Here again it is apparent that the degree of correlation between nitrification behavior and solubility pattern and activity index is considerably greater than that for neutral permanganate. The nitrification index also is somewhat more closely correlated with the activity index than with the solubility pattern index. This results from the better correlation between WIN and nitrification in 3 weeks

Table IV. Correlation Coefficients between Type A Secondary Factors^a

Factor	Neutral Permanganate-Insoluble Nitrogen, PIN	Primary plus Secondary Solubility, A + B _x	Hot Water-Insoluble Nitrogen, HWIN
Nitrification in 15 weeks, N ₁₅	-0.69	+0.86	-0.89
Neutral permanganate-insoluble nitrogen, PIN	...	-0.73	+0.88
Primary plus secondary solubility, A + B _x	-0.89

^a All correlations significant at 1% level.

Table V. Correlation Coefficients between Type B Secondary Factors^a

Factor	Water-Insoluble Neutral Permanganate-Soluble Nitrogen, WIN-PIN	Secondary Solubility, B _x	Water-Insoluble Hot Water-Soluble Nitrogen, WIN-HWIN
Increase in nitrification between 3 and 15 weeks, N ₁₅ - N ₃	+0.66	+0.93	+0.86
Water-insoluble neutral permanganate-soluble nitrogen, WIN-PIN	...	+0.55	+0.79
Secondary solubility, B _x	+0.92

^a All correlations significant at 1% level.

Table VI. Correlation Coefficients between Index Factors^a

Index	Neutral Permanganate, 100(WIN-PIN) / WIN	Solubility, Pattern, 100 B _x / 100 - A	Activity (AI), 100(WIN-HWIN) / WIN
Nitrification, $\frac{100(N_{15} - N_3)}{100 - N_3}$	+0.65	+0.88	+0.90
Neutral permanganate Solubility pattern	...	+0.58	+0.74
	+0.89

^a All correlations significant at 1% level.

than that between the primary solubility, A, and N_3 . The scatter diagram between the nitrification index and AI (Figure 5) shows that a nitrification index ≈ 30 generally is associated with an AI ≈ 40 . This minimum nitrification index is substantially equivalent to the values assumed for its component factors—i.e., $N_{15} - N_3 \approx 25$ and $N_3 \approx 15$, or $N_{15} - N_3 \approx 30$ for $N_3 = 0$.

Similarly, AI ≈ 40 is equivalent to HWIN ≈ 45 and WIN ≈ 75 , or to HWIN ≈ 60 for WIN = 100. The scatter diagram between the neutral permanganate activity and the nitrification index ($r = 0.65$) shows that the equivalent permanganate activity ≈ 80 . This value also is in agreement with PIN ≈ 15 for WIN ≈ 75 , or with PIN ≈ 20 for WIN = 100.

Figure 3. Relation between nitrification in 3 weeks and water-insoluble nitrogen

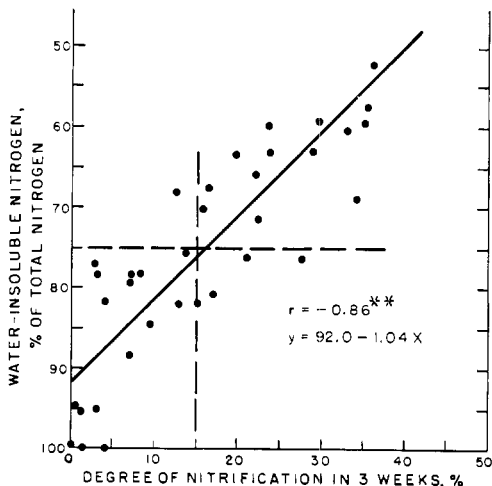


Figure 4. Relation between increase in nitrification between 3 and 15 weeks and hot water-soluble nitrogen

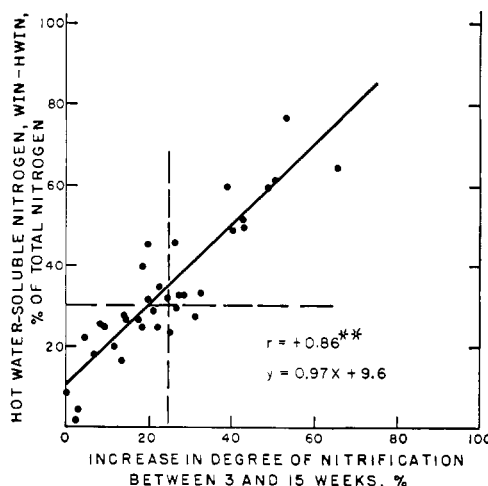
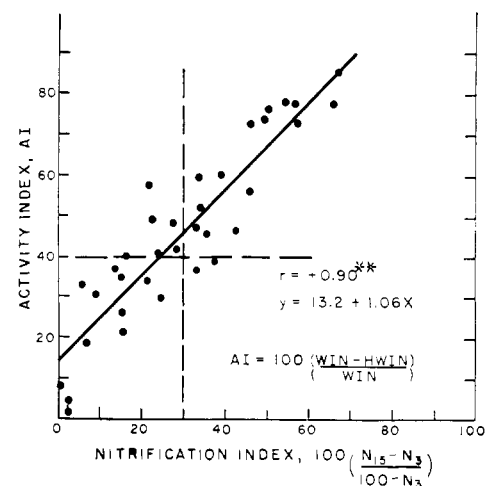


Figure 5. Relation between nitrification index and activity index



General Twenty-three of the 35 samples (66%) were correctly rated in relation to the nitrification index by all three solubility index procedures, 24 (69%) by neutral permanganate activity, 28 (80%) by activity index, *AI*, and 30 (86%) by the solubility pattern index.

Of the 12 samples incorrectly rated by one or more of the solubility indexes, 11 (92%) were incorrectly rated by neutral permanganate activity, seven (58%) by activity index, and five (42%) by the solubility pattern. Of these 12, nine exhibited inferior nitrification characteristics, with two of the nine being borderline cases with values of 27.7 and 28.6, respectively. Of the three exhibiting acceptable nitrification indexes, two were borderline cases with values of 33.1 and 33.2.

Of the eight nonborderline cases, one was superior, with a nitrification index of 37.3. All solubility indexes for this sample were borderline but slightly below the stated minima. The other seven nonborderline cases were definitely inferior with nitrification indexes in the

range 5.7 to 22.7. Six of the seven were correctly rated by the solubility pattern index, four by the activity index, and none by the neutral permanganate activity

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GROWTH REGULATORS

Amino Acid Derivatives of 4-Chlorophenoxyacetic Acid and Their Plant-Regulating Effects in Preliminary Screening Tests

C. F. KREWSON, T. F. DRAKE,
C. H. H. NEUFELD, and
T. D. FONTAINE

Eastern Regional Research
Laboratory, Philadelphia 18, Pa.

J. W. MITCHELL and
W. H. PRESTON, Jr.
Horticultural Crops Research Branch,
Agricultural Research Service,
Beltsville, Md.

Continued interest in elucidating the mode of action of plant-growth regulators and in compounds having greater selective activity has led to the preparation and evaluation of derivatives of amino acids and other plant constituents. A series of new D-, L-, and DL-amino acid derivatives of 4-chlorophenoxyacetic acid was prepared and screened for plant-growth regulating activity. In general, the derivatives of DL- and L-amino acids proved to be active plant-growth regulators when tested on Black Valentine bean, sunflower, cucumber, barley, and corn plants; those of D-amino acids were less active and more selective. A notable exception to this generalization was the D-alanine derivative, which was as active as the L-isomer. The reason for the high activity of the D-alanine derivative has not been explained, but it is recognized that certain microorganisms are able to utilize D-alanine.

CRITICAL EVALUATION OF 4-CHLOROPHENOXYACETIC ACID (referred to sometimes as 4-CIPOA, CPA, 4-C, and Parachloro) as a herbicide is difficult. Results of commercial testing have not been sufficiently conclusive to justify specific recommendations for herbicidal use. The activity of 4-chlorophenoxyacetic acid in this respect requires further investigation (5). It has been stated (19), however, that the use of this compound has not been as great as 2,4-dichloro- or 2,4,5-trichlorophenoxyacetic acid because its action is milder.

As a selective growth regulator, 4-chlorophenoxyacetic acid appears to hold forth considerable promise. Weintraub, Brown, and Throne (24) recently reported that the compound has high formative effects as measured by tests of molar leaf area repression activity (MOLARA).

Zimmerman and Hitchcock (29) were among the first to demonstrate the growth-modifying properties of 4-chlorophenoxyacetic acid. They described this compound as less active than 2,4-dichlorophenoxyacetic acid in inducing

cell elongation of tomato, as having ability to induce adventitious roots, and ability to induce parthenocarp when applied to flowers of tomato and cucumber. Marre and Murneek (17) found that 4-chlorophenoxyacetic acid, applied to the cut surface of the style of emasculated tomato flowers, produced effects similar to those induced by pollination and fertilization—i.e., it stimulated the accumulation of starch and sugar. Moore and Thomas (15) state that 4-chlorophenoxyacetic acid appears to be a practical aid to growers