

19,789—a large difference of 364%.

Significant interaction data for variety \times growth rate for dry matter and yield, and harvest \times growth rate for oxalic acid and dry matter content and yield are not given because their inclusion would not have added any pertinent information.

Assuming the possibility of lowering the oxalate content by crossbreeding, a study of this type was initiated. When a number of foreign introductions were screened for oxalate content, several proved to be low in oxalates. These low-oxalate introductions were crossed with standard varieties in an attempt to lower the oxalate content of the latter. This work is just getting under way, and no conclusive results have been obtained at this time.

Acknowledgment

The authors express their appreciation to Jean Dickenson, Biochemistry and Nutrition Department, for her able assistance in analyzing the samples; to C. Y. Kramer, Statistics Department,

for the statistical planning of the study and analysis of the data; and to R. E. Webb, Crops Research Division, U. S. Department of Agriculture, Beltsville, Md., for furnishing the spinach seed used in this study and for cooperating in the aforementioned current crossbreeding program.

Literature Cited

- (1) Bassalik, K., *Verhandl. Schweiz Naturforsch. Ges.* **99**, 226-7 (1918).
- (2) Canterbury Agricultural College, Lincoln, New Zealand, Dept. Sci. Ind. Research, 11th Ann. Rept., 81-5, 1954.
- (3) Duncan, D. B., *Biometrics* **11**, 1 (1955).
- (4) Eheart, James F., Hurst, David C., *J. Assoc. Offic. Agr. Chemists* **45**, 98 (1962).
- (5) Fairbanks, B. W., Mitchell, H. H., *J. Nutrition* **16**, 79 (1938).
- (6) Fincke, M. L., Garrison, E. A., *J. Home Econ.* **28**, 572 (1936).
- (7) Fincke, M. L., Sherman, H. C., *J. Biol. Chem.* **110**, 421 (1935).
- (8) Grütz, W. Z., *Pflanzenernähr. Düng. Bodenk.* **62**, 24-30 (1953).

- (9) Imada, S., et al., *Repts. Sci. Living, Osaka City Univ.* **2**, 25-30 (1954).
- (10) Kohman, E. F., *J. Nutrition* **13**, 233 (1939).
- (11) Lovelace, F. E., Liu, C. H., McKay, C. M., *Arch. Biochem.* **27**, 48-56 (1950).
- (12) McLaughlin, Laura, *J. Biol. Chem.* **74**, 455 (1927).
- (13) Myers, A. T., *J. Agr. Research* **74**, 33-47 (1947).
- (14) Pierce, Elwood C., Appleman, C. O., *Plant Physiol.* **18**, 224 (1943).
- (15) Pucher, Geo. W., Wakeman, A. J., Vickery, H. B., *J. Biol. Chem.* **119**, 523-34 (1937).
- (16) Speirs, M., *J. Nutrition* **17**, 557 (1939).
- (17) Talapatra, S. K., Ray, S. C., Sen, K. C., *J. Agr. Sci.* **38**, 163 (1948).
- (18) Tisdale, F. T., Drake, T. G. H., *J. Nutrition* **16**, 613 (1942).
- (19) Van Itallie, L., Lemkes, H. J., *Pharm. Weekblad* **54**, 1234-8 (1917).
- (20) Wooster, Harold A., Jr., "Nutritional Data," 2nd ed., p. 124, H. J. Heinz Co., Pittsburgh, Pa., 1954.

Received for review June 19, 1961. Accepted September 29, 1961.

NUTRIENTS IN MARKETED FERTILIZERS

Calcium, Magnesium, and Sulfur Contents of Mixed Fertilizers Marketed in 1949-50 and in 1955-56

W. M. HOFFMAN, R. J. FERRETTI, and K. G. CLARK

U. S. Fertilizer Laboratory, Soil and Water Conservation Research Division, U. S. Department of Agriculture, Beltsville, Md.

The trend to higher analysis fertilizers often is regarded as signifying an accompanying decrease in the calcium, magnesium, and sulfur contents of the nation's fertilizers. These secondary elements were determined on 425 and 491 samples, of mixed fertilizers marketed during the 1949-50 and 1955-56 fertilizer seasons. Although the average calcium, magnesium, and sulfur contents decreased 5.3, 12.8, and 4.8%, respectively, in this 6-year interval, they remained at substantially the same levels as in earlier years. The ratios of the secondary nutrients to nitrogen, phosphorus, and potassium decreased appreciably, however, because of the trend to high-analysis mixtures. The tonnage of secondary elements applied in mixtures during the 1955-56 season exceeded that applied in the 1949-50 season, since the increase in tonnage of marketed fertilizers more than offset the decrease in the average contents of the secondary elements.

THE TREND to higher analysis fertilizers often is regarded as signifying an accompanying decrease in the calcium, magnesium, and sulfur contents of the nation's fertilizers. Since soil additions of these elements are needed in many areas, decreases in the quantities present in fertilizers may result in their inferior performance under crops. Reliable information, therefore, is needed on this aspect of fertilizer composition.

Surveys of solid mixed fertilizers marketed in the United States during the 1949-50 and the 1955-56 fertilizer

seasons were conducted to obtain information on their physical and chemical characteristics (1-4). Thus, 916 mixed fertilizers, representative of technological conditions at the time of their production, were available for determining the trend in secondary nutrient content over the 1949-1955 period. The 425 samples collected in 25 states for the 1949-50 survey represented the products of 157 manufacturers and were marketed in 91 grades and 58 plant-nutrient ratios. Of these samples 23 were N-P, five N-K, 24 P-K, and 373 N-P-K mixtures. The

491 samples collected in 35 states for the 1955-56 survey represented the products of 160 manufacturers and were marketed in 90 grades and 60 plant-nutrient ratios. Of these samples, 17 were N-P, five N-K, 26 P-K, and 443 N-P-K mixtures.

Analytical Methods

Solutions for the determination of calcium, magnesium, and sulfur were prepared by digesting a portion of the ground fertilizer with a 3 to 1 concentrated nitric-hydrochloric acid mixture.

Table I. Comparison of Calcium, Magnesium, and Sulfur Contents of Mixed Fertilizers in 1949-50 and 1955-56, by Regions and State

Region and State	No. of Samples		Calcium, %			Magnesium, %			Sulfur, %				
	1949-50 Survey	1955-56 Survey	1949-50 Survey	1955-56 Survey	1949-50 Survey	1955-56 Survey	1949-50 Survey	1955-56 Survey	1949-50 Survey	1955-56 Survey			
	Survey	Survey	Range	Mean	Range	Mean	Range	Mean	Range	Mean			
New England													
Connecticut	9	3	3.07-13.70	9.83	8.90-12.78	10.26	0.49-1.80	1.17	0.30-1.37	1.02-11.26	6.94	3.08-9.34	6.19
Maine	15	8	4.63-14.12	10.57	7.86-14.83	10.63	0.64-2.53	1.66	0.04-1.44	1.13-12.30	8.49	6.91-11.40	9.31
Massachusetts	10	5	4.47-15.92	11.21	8.86-12.94	10.90	0.86-2.56	1.78	0.24-2.29	2.22-10.88	7.40	6.52-11.65	8.57
	34	16		10.56		10.64		1.57			7.76		8.49
Middle Atlantic													
Delaware	12	6	10.68-16.73	13.94	10.58-16.15	13.10	0.02-2.68	1.20	0.00-2.60	6.91-13.99	9.55	6.23-9.48	8.24
Maryland	11	8	10.73-15.44	13.82	11.31-14.56	12.00	0.08-2.38	1.18	0.00-1.72	6.68-10.67	8.89	7.52-11.33	9.38
New Jersey	14	16	5.99-15.20	12.27	10.00-14.97	12.02	0.26-2.12	1.27	0.25-2.92	5.82-12.41	9.27	5.34-11.74	8.89
New York	13	18	10.87-18.09	14.21	7.73-15.95	12.41	0.04-2.68	1.29	0.20-2.58	5.12-11.38	8.87	4.06-14.08	8.77
Pennsylvania	50	59		13.52		12.46		1.24			9.15		8.90
South Atlantic													
Florida	35	36	1.13-15.89	8.61	2.78-15.73	8.98	0.22-4.51	1.86	0.03-6.71	1.71-11.90	6.74	3.08-14.73	7.41
Georgia	27	39	6.00-17.97	11.33	0.97-16.62	11.46	0.00-2.45	0.87	0.00-3.54	5.20-8.49	6.66	0.00-9.96	6.90
North Carolina	36	50	7.80-16.79	13.46	0.26-17.10	12.08	0.98-4.31	2.11	0.18-3.33	0.00-10.45	8.15	5.84-17.60	8.37
South Carolina	24	21	11.25-18.68	14.28	8.95-18.12	12.84	0.46-2.99	1.85	0.24-3.14	6.46-11.93	8.26	4.76-9.40	7.62
Virginia	22	22		14.26	5.52-15.62	13.18			0.52-2.81			4.26-14.58	8.17
	122	168		11.76		11.51		1.71			7.44		7.70
East South Central													
Alabama	18	23	11.10-17.78	14.48	11.53-22.10	14.70	0.39-3.46	2.27	0.50-3.62	6.81-11.22	8.89	6.10-9.48	7.50
Kentucky	19	14	9.66-19.01	14.49	8.10-16.36	13.05	0.24-2.53	1.32	0.07-1.78	5.17-12.66	9.59	6.50-14.32	9.31
Mississippi	11	9	8.48-19.14	13.50	11.94-16.17	14.61	0.89-3.08	2.08	0.29-3.26	7.92-11.40	9.43	7.33-11.56	8.81
Tennessee	16	16		14.26	8.72-16.91	12.83			0.04-5.32			4.31-13.12	8.99
	48	62		14.26		13.83		1.85			9.29		8.48
West South Central													
Arkansas	6	6	8.95-15.50	11.76	6.61-17.93	11.44	0.03-2.05	0.89	0.20-4.00	8.51-12.05	10.13	5.76-7.69	6.76
Louisiana	8	6		11.76	6.37-17.03	11.57			0.00-2.32			7.56-11.31	9.30
Oklahoma	15	2	9.03-17.02	12.98	11.61-12.23	11.92	0.00-2.31	0.80	1.19-1.32	6.33-17.86	9.86	7.20-11.69	9.44
Texas	23	14		12.56		11.56		0.83			9.95		8.23
East North Central													
Illinois	40	37	10.30-20.56	14.31	5.71-14.17	10.79	0.00-7.14	0.41	0.14-1.22	2.32-11.82	7.81	5.64-13.91	8.78
Indiana	24	33	10.34-17.59	14.89	7.56-17.59	11.89	0.19-7.36	1.42	0.00-1.37	3.62-11.19	8.02	3.74-14.31	7.36
Michigan	17	13	8.29-18.50	14.29	5.91-15.38	12.27	0.16-2.40	1.42	0.18-2.88	3.62-11.19	8.02	4.95-12.66	8.61
Ohio	17	13		14.29	8.10-14.63	10.76		1.48	0.55-2.06	2.35-12.53	8.25	4.00-13.39	8.39
Wisconsin	81	111		14.48		11.90		0.93			7.96	2.65-14.28	6.28
West North Central													
Iowa	16	16		12.93	1.20-18.80	11.25			0.00-2.66			2.86-15.52	8.82
Kansas	14	9	3.19-16.22	10.54	2.50-13.47	8.45	0.14-4.14	1.11	0.33-0.58	0.61-13.26	5.75	3.89-12.72	9.66
Minnesota	16	16	12.85-18.13	15.02	9.65-15.67	11.45	0.16-2.40	1.42	0.00-2.26	7.58-10.72	8.88	0.17-11.15	6.21
Missouri	3	3		12.93	8.94-12.45	10.68		1.28	0.21-0.39			3.87-13.87	7.64
Nebraska	30	47		12.93		11.34		0.80			7.42	4.16-12.93	7.13
Mountain													
Arizona	16	1	2.48-14.84	8.57		11.06	0.07-2.08	0.80		4.98-24.12	14.49		8.50
Colorado	3	3		8.57		11.06							14.99
Idaho	4	4		8.57	2.53-7.58	5.64			0.00-0.52				6.16-14.12
Montana	4	2	7.21-13.06	9.38	4.48-10.92	7.70	0.00-1.74	0.69	0.00-0.73	5.92-21.41	12.38	4.38-7.29	5.84
Utah	20	10		8.73		7.63		0.78	0.39-0.74		14.07		10.38

Pacific	15	4	2.95-12.24	7.39	3.11-7.23	5.03	0.00-0.49	0.21	0.18-0.59	0.44	3.23-20.53	11.74	12.64-21.48	16.72
California	2	...	8.16-12.15	10.16	0.32-0.53	0.42	7.60-10.92	9.26
Oregon	17	4	7.72	7.72	...	5.03	0.23	0.23	...	0.44	11.45	11.45	16.72	
United States	425	491	1.13-20.56	12.49	0.26-22.10	11.83	0.00-7.36	1.33	0.00-6.71	1.16	0.00-24.12	8.58	0.00-21.48	8.17

Table II. Comparison of Calcium, Magnesium, and Sulfur Contents of Mixed Fertilizers in 1949-50 and 1955-56, by Regions and Class

Region and Fertilizer Classification	No. of Samples		Calcium, %			Magnesium, %			Sulfur, %			Average N-P ₂ O ₅ -K ₂ O grade, %									
	1949-1955-56		1949-50 Survey			1955-56 Survey			1949-50 Survey			1955-56 Survey			1949-50 survey			1955-56 survey			
	Survey	Range	Mean	Range	Mean	Survey	Range	Mean	Survey	Range	Mean	Survey	Range	Mean	Survey	Range	Mean	Survey	Range	Mean	
New England	34	16	3.07-15.92	10.56	7.86-14.83	10.64	0.49-2.56	1.57	0.04-2.29	0.91	1.02-12.30	7.76	3.08-11.65	8.49	5.38-9.76	10.44	5.81-10.50	11.75	4	-10	-0
All mixtures	1	...	9.88-15.92	12.34	8.90-14.83	11.86	0.49-1.36	0.83	0.04-0.70	0.37	4.07-9.12	5.76	3.08-9.13	6.10	0	-18	-18	0	-14.50	-22.00	0
N-P grades	3	2	3.07-15.68	10.28	7.28-12.94	10.47	0.64-2.56	1.67	0.24-2.29	0.99	1.02-12.30	7.97	6.14-11.65	8.83	5.97-8.93	10.03	6.64-9.93	10.29	0	0	0
P-K grades	30	14	5.99-18.09	13.52	7.73-17.02	12.46	0.02-2.68	1.24	0.00-3.41	1.10	5.12-13.99	9.15	4.06-14.08	8.90	4.08-11.04	7.54	5.61-10.81	9.14	0	-14	-7
Middle Atlantic	2	3	16.12-17.10	16.61	11.73-15.49	13.11	0.65-0.96	0.80	1.20-2.92	1.79	9.13-9.28	9.20	4.06-9.48	6.29	0	-14	-7	0	-18.00	-18.00	0
All mixtures	48	56	5.99-18.09	13.39	7.73-17.02	12.43	0.02-2.68	1.26	0.00-3.41	1.06	5.12-13.99	9.15	6.23-14.08	9.04	4.25-10.92	7.56	5.91-10.43	8.66	0	0	0
N-P-K grades	122	168	1.13-18.68	11.76	0.26-18.12	11.51	0.00-4.51	1.71	0.00-6.71	1.53	0.00-11.93	7.44	0.00-17.60	7.70	4.14-8.38	6.32	4.63-9.18	8.45	4	-16	-0
All mixtures	1	...	1.13-7.80	5.56	0.80-9.88	4.51	1.49-4.51	3.25	0.00-6.71	2.28	0.00-11.90	10.00	0.00-17.60	8.35	10.40	0	-10.40	11.60	0	-12.00	0
N-P grades	5	5	17.79	17.79	11.35-15.73	14.08	...	2.71	0.74-1.16	0.98	...	7.54	4.26-8.89	7.63	0	-12	-12	0	-14.80	-15.60	0
P-K grades	1	5	4.00-17.79	11.92	0.26-18.12	11.65	0.00-4.31	1.63	0.03-4.77	1.52	1.71-11.93	7.47	3.30-14.73	7.68	3.90-8.64	6.15	4.09-9.30	8.11	0	0	0
N-P-K grades	115	158	8.48-19.14	14.26	8.10-22.10	13.83	0.24-3.46	1.85	0.04-5.32	1.73	5.17-12.66	9.29	4.31-14.32	8.48	4.38-9.73	5.54	4.26-10.13	8.39	0	0	0
East South Central	2	4	18.48-19.01	18.74	13.43-15.09	14.52	0.67-1.63	1.15	0.22-0.96	0.54	7.58-9.60	8.59	6.47-9.47	7.68	0	-13.00	9.50	0	-14.00	-14.00	0
All mixtures	46	58	8.48-19.14	14.06	8.10-22.10	13.78	0.24-3.46	1.88	0.04-5.32	1.81	5.17-12.66	9.32	4.31-14.32	8.54	4.57-9.59	5.37	4.55-9.86	8.00	0	0	0
N-P-K grades	23	14	8.95-17.02	12.56	6.37-17.93	11.56	0.00-2.31	0.83	0.00-4.00	1.18	6.33-17.86	9.95	5.76-11.31	8.23	5.17-10.35	4.96	6.07-11.29	9.36	0	0	0
All mixtures	2	1	10.22-12.97	11.60	...	11.61	0.66-1.20	0.93	...	1.19	9.94-17.86	13.90	...	11.69	0	-11.00	0	10.00	-20.00	0	0
N-P grades	1	...	8.95-16.27	12.43	6.37-17.93	11.56	0.00-2.31	0.81	0.00-4.00	1.18	6.33-12.36	9.57	5.76-11.31	7.96	0	-14	-7	0	0	0	
N-P-K grades	20	13	8.29-20.56	14.48	5.71-17.59	11.90	0.00-7.36	0.93	0.00-2.88	0.76	2.32-12.53	7.96	2.65-14.31	7.87	2.36-12.69	9.00	4.28-13.22	14.16	0	0	0
West North Central	12	8	10.30-20.56	15.21	8.52-17.59	11.80	0.53-2.68	1.13	0.30-2.06	0.83	4.02-9.90	7.31	2.65-8.69	4.76	0	-14.00	13.00	0	-17.50	-21.25	0
All mixtures	69	103	8.29-18.50	14.35	5.71-17.01	11.91	0.00-7.36	0.90	0.00-2.88	0.75	2.32-12.53	8.07	3.56-14.31	8.11	2.77-12.43	8.30	4.61-12.88	13.61	0	0	0
N-P-K grades	30	47	3.19-18.13	12.93	1.20-19.60	11.34	0.14-4.14	1.28	0.00-2.66	0.45	0.61-13.26	7.42	0.17-15.52	7.86	3.60-14.97	8.60	7.04-16.95	9.36	0	0	0
All mixtures	...	9	9.00-16.80	13.55	8.94-16.53	12.08	...	0.20-0.58	0.34	3.89-12.93	8.82	0	-21.33	10.67	0	10.00	-23.30	0	0
N-P grades	3	4	3.19-18.13	12.86	1.20-19.60	11.05	0.14-2.40	1.17	0.00-2.66	0.47	0.61-13.26	7.86	2.86-15.52	8.08	4.00-14.26	8.37	7.09-14.91	11.29	0	0	0
N-P-K grades	27	34	2.48-14.84	8.73	2.53-14.44	7.63	0.00-2.08	0.78	0.00-0.74	0.33	4.98-24.12	14.07	4.38-19.99	10.38	9.30	14.35	1.15	9.10	-16.90	-2.50	0
Mountain	16	5	3.03-14.84	9.18	2.53-14.44	8.72	0.00-1.76	0.62	0.00-0.68	0.25	4.98-24.12	14.95	6.16-19.99	11.94	10.06	14.56	0	10.60	-21.00	0	0
All mixtures	4	5	2.48-13.06	6.95	3.29-10.92	6.54	0.96-2.08	1.44	0.03-0.74	0.41	5.92-20.20	10.56	4.38-14.12	8.82	6.50	13.50	5.75	7.60	-12.80	-5.00	0
N-P grades	17	4	2.95-12.24	7.72	3.11-7.23	5.03	0.00-0.53	0.23	0.18-0.59	0.44	3.23-20.53	11.45	12.64-21.48	16.72	8.59	9.65	5.76	12.75	-8.75	-2.25	0
All mixtures	3	2	2.95-10.89	5.74	3.11-3.69	3.40	0.00-0.26	0.17	0.18-0.59	0.36	8.77-20.53	13.69	19.92-21.48	20.70	14.67	11.33	0	16.50	-8.50	0	0
N-P grades	14	2	3.21-12.24	8.17	6.10-7.23	6.66	0.00-0.53	0.24	0.44-0.59	0.52	3.23-18.90	10.97	12.64	12.86	7.74	7.29	9.29	7.00	9.00	-9.00	-4.50
N-P-K grades	425	491	1.13-20.56	12.49	0.26-22.10	11.83	0.00-7.36	1.33	0.00-6.71	1.16	0.00-24.12	8.58	0.00-21.48	8.17	4.38	10.72	7.06	4.86	-11.42	-9.91	0
All mixtures	23	17	2.95-18.68	9.55	2.53-16.53	10.04	0.00-1.80	0.65	0.00-1.19	0.37	4.98-24.12	14.16	3.89-21.48	11.30	9.96	13.70	0	11.0	-20.70	0	0
N-P grades	5	5	1.13-7.80	5.56	0.80-9.88	4.51	1.49-4.51	3.25	0.00-6.71	2.28	0.00-11.90	6.18	0.00-17.60	8.35	10.40	0	-10.40	11.60	0	-12.00	0
N-K grades	24	26	9.00-20.56	15.24	8.52-14.52	12.87	0.49-4.14	1.27	0.04-2.92	0.84	0.69-9.90	7.00	0.17-9.48	5.90	0	-15.25	-13.08	0	-16.70	-18.50	0
P-K grades	373	443	2.48-19.14	12.59	0.26-22.10	11.92	0.00-7.36	1.35	0.00-5.32	1.20	0.61-20.20	8.37	2.86-15.52	8.18	4.23	10.39	7.06	4.83	-10.88	-9.76	0
N-P-K grades																					

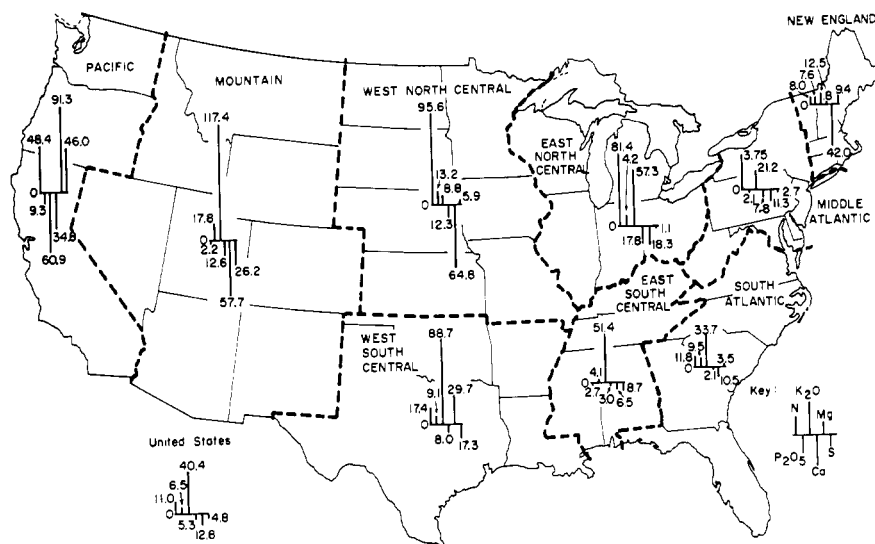


Figure 1. Changes in nutrient content of mixed fertilizers between 1949-50 and 1955-56 in per cent of 1949-50

One portion of the acid solution was used to determine calcium and magnesium and a second portion to determine sulfur by the gravimetric BaSO₄ method. The portion used for determination of calcium and magnesium was treated with sodium molybdate to complex the phosphorus and the phosphomolybdo complex was removed by repeated extraction with a 1 to 1 1-butanol-chloroform mixture (5). Total calcium and magnesium was titrated by EDTA at pH 10 using Eriochrome Black T as indicator in one portion of the phosphorus-free extract, and calcium was titrated by EDTA at pH 12.5 using calcon as indicator in another portion. All titrations were made spectrophotometrically with a Sargeant-Malmstadt Spectro-Electro titrator (6).

Analytical Results

Changes in the average nitrogen, P₂O₅, K₂O, calcium, magnesium, and sulfur contents of mixed fertilizers in 1955-56 in comparison with those in 1949-50 are shown by regions in Figure 1. The nitrogen, P₂O₅, and K₂O contents of all mixed fertilizers increased from 4.38 to 4.86, from 10.72 to 11.42, and from 7.06 to 9.91%, respectively. The corresponding percentage increases were 11.0, 6.5, and 40.4. The average nitrogen content increased in all regions except the East South Central and the Mountain, with the greatest increases occurring in the West North Central (95.6%) and East North Central (81.4%) regions. The average P₂O₅ content increased in all regions except the Middle Atlantic and Pacific. The average K₂O content increased in all regions except the Pacific, with the largest increases occurring in the Mountain (117.4%), West South Central (88.7%), East North Central (57.3%), and East South Central (51.4%) regions.

The average calcium, magnesium, and sulfur contents for all mixed fertilizers decreased between 1949-50 and 1955-56 from 12.49 to 11.83, from 1.33 to 1.16, and from 8.58 to 8.17%, respectively. The corresponding percentage decreases were 5.3, 12.8, and 4.8. Analytical data for each nutrient are summarized in relation to regions, states, and year in Table I, and to regions, grades, and year in Table II. A summary of the average N-P₂O₅-K₂O grades for each classification is included in Table II.

Calcium. In the six-year interval between the surveys the average calcium content of all mixed fertilizers decreased in all regions except New England. The largest decreases were in the East North Central (17.8%), West North Central (12.3%), and Pacific (34.8%) regions. The decreases in the West South Central and Middle Atlantic regions were 8.0 and 7.8%, respectively. The East South Central (3.0%) and South Atlantic (2.1%) regions showed only small decreases. The average calcium content increased 0.8% in the New England region.

In the 22 states from which samples were collected for both surveys, the average calcium contents decreased 6.2%. Seven of these states, however—Minnesota (West North Central), Connecticut and Maine (New England), Florida and Georgia (South Atlantic), and Alabama and Mississippi (East South Central)—exhibited increases.

The N-P-K mixtures exhibited a decrease of 5.3% in average calcium content, the N-K mixtures a decrease of 18.9%, and the P-K mixtures a decrease of 15.6%. The average calcium content of the N-P mixtures increased 5.1%. The average calcium content of the N-P-K mixtures decreased in every region except New England and also in the P-K mixtures in all regions (no samples

Table III. Average Calcium Content of Mixed Fertilizers for 1900-55

Year	Calcium, %
1900	11.42
1910	10.26
1920	11.34
1925	11.13
1929	10.90
1935	11.42
1939	11.04
1941	11.41
1944	11.95
1945	12.20
1949	12.49
1955	11.83

Table IV. Average Magnesium Content of Mixed Fertilizers for 1910-55

Year	Magnesium, %
1910	1.37
1930	0.60
1937	1.17
1945	1.25
1949-50	1.33
1955-56	1.16

taken in Mountain and Pacific regions in either survey and no samples in West South Central region in 1955-56 survey). Even though the N-P mixtures showed an over-all increase in calcium content, there was a 13.1% decrease in the West South Central, Mountain, and Pacific regions, which were represented by samples in both survey years.

The average calcium contents of mixed fertilizers as determined in the two surveys are compared in Table III with similar information cited by Mehring (7) for 1900-45. The data indicate that little or no change has occurred in the calcium content of mixed fertilizers since 1900.

Magnesium. In the six-year interval between the surveys the average magnesium content of all mixed fertilizers decreased in all regions except the West South Central and the Pacific. The largest decreases were in the West North Central (16.7%), the Middle Atlantic (11.3%), the South Atlantic (10.5%), and the East South Central (6.5%) regions. The average magnesium content increased in the West South Central and the Pacific regions by 42.2 and 91.3%, respectively.

In the 22 states common to both surveys, the average magnesium content decreased by 13.8%. Six states showed an increase, but only two (California and Indiana) were in regions other than the Middle Atlantic (Maryland), the South Atlantic (Florida and Georgia), and the East South Central (Mississippi).

The N-P-K mixtures showed a decrease of 11.1% in average magnesium content, the N-P mixtures a decrease of

Table V. Distribution of Calcium, Magnesium, and Sulfur Contents of Mixed Fertilizers in 1949-50 and 1955-56 in Relation to Nitrogen Grade

Nitrogen Grade, %	Samples																		
	1949-50 Survey			1955-56 Survey			1949-50 Survey			1955-56 Survey									
	No.	Weighted av. N-P ₂ O ₅ -K ₂ O grade, %	No. N-P ₂ O ₅ -K ₂ O grade, %	Weighted av.	Mean	Range	Mean	Range	Mean	Range	Mean	Range							
0	24	0	-15.33-12.25	26	0	-16.65-18.15	9.00-20.56	15.24	8.52-14.52	12.87	0.49-4.14	1.27	0.04-2.92	0.84	0.69-9.90	7.00	0.17-9.48	5.90	
2	53	2	-11.79-6.04	15	2	-12.00-11.20	6.06-18.50	15.08	12.29-16.36	14.42	0.10-7.36	1.42	0.07-1.58	0.91	3.32-11.19	8.20	7.42-9.29	7.92	
3	79	3	-11.08-7.96	121	3	-10.69-10.61	8.29-18.09	13.58	7.84-19.60	12.99	0.00-3.14	1.27	0.00-5.32	1.33	2.35-13.99	8.06	4.14-13.12	7.94	
4	116	4	-10.26-6.21	116	4	-11.15-9.27	4.00-18.68	12.57	6.32-17.10	12.41	0.00-4.07	1.27	0.00-4.77	1.21	0.61-11.77	7.77	3.92-14.73	7.24	
5	58	5	-9.91-7.78	83	5	-11.20-9.90	4.80-19.14	12.28	4.86-17.93	11.78	0.00-3.07	1.33	0.00-4.00	1.15	0.71-12.36	8.45	2.86-14.32	8.12	
6	45	6	-9.42-6.40	49	6	-10.12-7.53	4.64-17.26	11.56	3.29-22.10	11.89	0.08-3.54	1.86	0.00-4.08	1.43	1.02-20.33	9.18	3.80-13.50	8.69	
8	17	8	-8.82-9.88	24	8	-13.83-8.75	3.07-11.17	7.46	2.78-13.95	9.56	0.03-4.51	1.36	0.00-6.71	1.53	1.13-16.66	9.62	3.87-13.87	8.00	
10	23	10	-12.43-3.17	37	10	-12.16-8.00	2.48-14.84	7.92	0.26-14.44	12.07	0.06-1.76	0.71	0.00-2.60	0.53	4.98-24.12	13.47	0.00-14.31	10.76	
Subtotal	415	4.18-10.83	7.09-471	4.52-11.48	9.97	2.48-20.56	12.62	0.26-22.10	12.03	0.00-7.36	1.36	0.00-6.71	1.19	0.00-2.70	0.55	0.00-21.41	13.11	3.08-21.48	12.31
Other grades ^a	10	12.70-5.60	2.70	20	12.85-10.30	8.10	1.13-15.68	7.02	0.80-12.03	6.11	0.00-4.31	1.17	0.00-2.70	0.55	0.00-21.41	13.11	3.08-21.48	12.31	
Total	425	4.38-10.72	7.06-491	4.86-11.42	9.91	1.13-20.56	12.49	0.26-22.10	11.83	0.00-7.36	1.33	0.00-6.71	1.16	0.00-24.12	8.58	0.00-21.48	8.17		

^a Eight other grades in 1949-50 survey and 10 other grades in 1955-56 survey.

Table VI. Distribution of Calcium, Magnesium, and Sulfur Contents of Mixed Fertilizers in 1949-50 and 1955-56 in Relation to P₂O₅ Grade

Phosphorus Grade, %	Samples																	
	1949-50 Survey			1955-56 Survey			1949-50 Survey			1955-56 Survey								
	No.	Weighted av. N-P ₂ O ₅ -K ₂ O grade, %	No. N-P ₂ O ₅ -K ₂ O grade, %	Weighted av.	Mean	Range	Mean	Range	Mean	Range	Mean	Range						
0	5	10.40-0	-10.40	5	11.60-0	-12.00	1.13-7.80	5.56	0.80-9.80	4.49	1.49-4.51	3.25	0.00-6.71	2.28	0.00-11.90	6.18	0.00-17.60	8.35
3	6	4.83-4	-7.00	3	8.67-4	-7.33	3.07-11.20	5.46	2.78-10.64	4.39	1.51-2.56	1.91	0.39-4.35	3.37	1.02-3.02	2.09	4.07-6.19	7.83
4	6	4.83-4	-7.00	3	8.67-4	-7.33	3.07-11.20	5.46	2.78-10.64	4.39	1.51-2.56	1.91	0.39-4.35	3.37	1.02-3.02	2.09	4.07-6.19	7.83
5	3	7.33-5	-6.00	2	5.00-5	-5.50	6.06-7.60	7.02	7.58-8.16	7.87	0.00-0.37	0.16	1.01-2.58	1.80	2.52-21.41	10.48	3.30-6.25	4.78
6	6	6.50-6	-6.00	2	5.00-5	-5.50	6.06-7.60	7.02	7.58-8.16	7.87	0.00-0.37	0.16	1.01-2.58	1.80	2.52-21.41	10.48	3.30-6.25	4.78
7	13	6.69-7	-5.31	6	6.67-7	-4.50	2.95-15.68	9.56	4.86-11.53	8.18	0.59-3.24	1.94	0.03-4.08	2.26	3.44-17.16	8.63	6.83-13.30	9.31
8	65	5.24-8	-5.88	57	5.28-8	-7.17	3.80-17.97	11.47	7.23-22.10	11.33	0.00-3.54	1.42	0.03-4.77	1.55	4.77-18.90	8.61	4.25-14.73	7.70
9	39	3.79-9	-7.62	65	3.31-9	-9.66	6.35-15.96	11.98	7.84-16.91	11.76	0.08-3.60	1.70	0.00-5.32	1.67	5.17-13.99	8.29	4.14-13.12	7.80
10	103	5.33-10	-6.46	131	5.63-10	-8.39	2.48-19.14	12.45	3.29-18.80	12.08	0.00-3.08	1.34	0.00-4.00	1.25	3.60-24.12	9.52	4.38-19.92	8.97
12	135	2.80-12	-7.13	121	3.92-12	-11.12	4.63-20.56	14.72	2.50-19.60	13.39	0.00-7.36	1.27	0.00-3.02	0.84	2.32-12.22	8.59	4.16-15.52	8.45
14	8	0.00-14	-7.88	11	1.64-14	-13.64	15.21-18.48	16.78	1.20-15.73	13.08	0.68-1.63	1.06	0.04-2.93	0.84	8.82-9.90	9.39	6.47-13.46	8.67
15	3	5.00-15	-11.67	3	10.00-15	-10.00	10.87-12.86	12.09	8.90-9.39	9.08	1.36-1.56	1.34	0.21-0.70	0.50	5.12-7.76	6.10	3.08-12.93	9.58
16	9	6.00-16	-9.33	28	4.80-16	-15.71	4.04-18.68	11.23	7.10-13.83	11.28	0.19-2.50	1.15	0.00-2.66	0.61	1.13-10.00	7.25	4.49-11.89	7.34
18	6	4.00-18	-9.00	3	5.33-18	-7.67	5.05-15.91	12.96	6.43-15.12	12.22	0.17-2.08	0.87	0.16-1.40	0.64	6.38-8.46	7.50	8.47-14.12	10.55
20	14	5.36-20	-7.86	33	4.39-20	-1.48	3.03-15.68	10.18	0.26-17.59	10.73	0.06-4.14	0.96	0.00-2.92	0.65	0.69-16.61	8.27	0.17-13.08	5.94
24	6	4.67-24	-10.00	7	7.43-24	-6.86	8.64-11.59	10.09	10.44-16.53	12.27	0.16-1.02	0.53	0.00-0.68	0.34	0.61-20.33	5.70	3.80-8.50	5.87
30	1	0	-30	1	6	-30	0	9.00	10.44-16.53	12.27	0.16-1.02	0.53	0.00-0.68	0.34	0.61-20.33	5.70	3.80-8.50	5.87
32	425	4.38-10.72	7.06-491	4.86-11.42	9.91	1.13-20.56	12.49	0.26-22.10	11.83	0.00-7.36	1.33	0.00-6.71	1.16	0.00-24.12	8.58	0.00-21.48	8.17	
Subtotal	425	4.38-10.72	7.06-491	4.86-11.42	9.91	1.13-20.56	12.49	0.26-22.10	11.83	0.00-7.36	1.33	0.00-6.71	1.16	0.00-24.12	8.58	0.00-21.48	8.17	
Other grades ^a	10	12.70-5.60	2.70	20	12.85-10.30	8.10	1.13-15.68	7.02	0.80-12.03	6.11	0.00-4.31	1.17	0.00-2.70	0.55	0.00-21.41	13.11	3.08-21.48	12.31
Total	425	4.38-10.72	7.06-491	4.86-11.42	9.91	1.13-20.56	12.49	0.26-22.10	11.83	0.00-7.36	1.33	0.00-6.71	1.16	0.00-24.12	8.58	0.00-21.48	8.17	

^a One 15-11-0 and 13-13-13 grade.

Table VII. Distribution of Calcium, Magnesium, and Sulfur Contents of Mixed Fertilizers in 1949-50 and 1955-56 in Relation to K₂O Grade

Potassium Grade, %	1949-50 Survey				1955-56 Survey				Calcium, %				Magnesium, %				Sulfur, %			
	Weighted av.		No. N-P ₂ O ₅ -K ₂ O grade, %		Weighted av.		No. N-P ₂ O ₅ -K ₂ O grade, %		Range		Mean		Range		Mean		Range		Mean	
	No.	N-P ₂ O ₅ -K ₂ O grade, %	No.	N-P ₂ O ₅ -K ₂ O grade, %	No.	N-P ₂ O ₅ -K ₂ O grade, %	No.	N-P ₂ O ₅ -K ₂ O grade, %	1949-50 Survey	1955-56 Survey	1949-50 Survey	1955-56 Survey	1949-50 Survey	1955-56 Survey	1949-50 Survey	1955-56 Survey	1949-50 Survey	1955-56 Survey	1949-50 Survey	1955-56 Survey
0	23	9.96-13.70	0	17	11.00-20.70	0	3	2.95-18.68	9.55	2.53-16.53	10.04	0.00-1.80	0.65	0.00-1.19	0.37	4.98-24.12	14.16	3.89-21.48	11.30	
3	3	4.00-9.00	3	3	4.00-9.00	3	3	6.35-12.67	10.45	8.90-12.23	10.04	1.92-3.60	2.49	0.88-1.88	1.47	6.64-9.04	7.89	5.88-8.16	7.28	
4	42	5.17-9.88	4	17	6.82-8.82	4	17	3.40-17.78	13.39	3.29-22.10	12.04	0.00-3.46	1.57	0.13-2.79	1.71	3.23-18.90	9.58	4.38-12.86	8.33	
5	40	5.08-9.32	5	28	5.21-9.68	5	28	2.48-19.14	11.86	6.10-17.93	12.01	0.00-3.49	1.40	0.00-4.00	1.48	2.78-20.20	8.79	3.92-14.12	8.37	
6	156	3.35-9.67	6	78	3.90-9.17	6	78	4.47-18.50	13.69	4.86-17.10	12.05	0.00-7.36	1.40	0.03-5.32	1.60	1.02-12.66	7.92	3.30-13.30	7.77	
7	22	3.14-10.73	7	18	4.22-9.72	7	18	10.06-18.48	14.27	10.34-17.02	11.47	0.59-2.60	1.36	0.91-3.62	2.12	5.56-10.90	8.82	6.10-9.49	7.72	
8	38	5.37-9.26	8	46	5.54-9.78	8	46	3.07-16.73	10.27	2.78-17.01	11.37	0.03-4.51	1.28	0.00-4.08	1.57	2.52-12.53	8.91	3.87-14.73	7.93	
9	8	4.12-13.50	9	22	3.14-9.86	9	22	10.60-15.91	13.27	8.95-15.12	12.21	0.17-2.42	1.08	0.37-2.94	1.60	6.38-10.66	8.32	5.64-10.32	8.47	
10	34	5.21-10.76	10	76	6.60-10.37	10	76	3.19-15.68	11.10	0.97-17.59	11.07	0.00-4.14	1.27	0.00-2.93	0.85	0.69-13.26	8.38	0.00-14.31	9.17	
12	43	3.53-12.30	12	106	4.10-11.99	12	106	1.13-20.56	12.63	2.50-19.60	13.06	0.00-3.24	1.14	0.00-6.71	0.92	0.61-16.66	8.01	3.80-15.52	8.32	
13	2	7.00-7.00	13	1	13-13	13	1	7.80-15.92	14.23	8.80-15.73	11.75	1.36-4.31	2.84	0.04-1.48	0.69	0.00-9.12	4.56	6.47-17.60	10.08	
14	2	3.67-18.00	14	3	5.00-10.00	14	3	9.00-10.87	10.04	10.01-12.59	11.27	1.40-1.88	1.70	0.48-1.09	0.79	0.89-9.55	5.19	7.28-14.32	11.96	
15	3	8.00-15.00	15	29	4.55-15.72	15	29	4.04-6.94	5.23	7.10-14.00	11.38	0.24-2.50	1.68	0.00-2.66	0.64	1.13-8.00	5.59	4.49-9.82	7.29	
16	4	3.00-9.00	16	5	3.00-9.00	16	5	9.48-12.73	11.34	9.48-10.93	10.09	0.93-1.66	1.30	0.17-1.23	0.63	5.84-6.12	5.98	5.10-6.39	5.72	
18	2	1.67-20.00	18	22	2.73-20.00	18	22	7.99-11.23	9.85	9.26-13.44	9.93	0.49-0.78	0.63	0.11-2.92	0.77	2.23-4.10	3.60	0.17-7.52	4.33	
20	4	1.67-20.00	20	5	3.00-9.00	20	5	7.84-10.52	9.25	7.84-10.52	9.25	
27	1	0	27	3	0.00-11.67	27	3	11.99	8.52-9.92	9.11	1.02	0.30-2.06	1.02	
30	425	4.38-10.72	30	491	4.86-11.42	30	491	1.13-20.56	12.49	0.26-22.10	11.83	0.00-7.36	1.33	0.00-6.71	1.16	0.00-24.12	8.58	0.00-21.48	8.17	
Total			Total			Total														

Table VIII. Distribution of Calcium, Magnesium, and Sulfur Contents of Mixed Fertilizers in 1949-50 and 1955-56 in Relation to Total Primary Nutrients

Total Primary Nutrient Grade, %	1949-50 Survey				1955-56 Survey				Calcium, %				Magnesium, %				Sulfur, %			
	Weighted av.		No. N-P ₂ O ₅ -K ₂ O grade, %		Weighted av.		No. N-P ₂ O ₅ -K ₂ O grade, %		Range		Mean		Range		Mean		Range		Mean	
	No.	N-P ₂ O ₅ -K ₂ O grade, %	No.	N-P ₂ O ₅ -K ₂ O grade, %	No.	N-P ₂ O ₅ -K ₂ O grade, %	No.	N-P ₂ O ₅ -K ₂ O grade, %	1949-50 Survey	1955-56 Survey	1949-50 Survey	1955-56 Survey	1949-50 Survey	1955-56 Survey	1949-50 Survey	1955-56 Survey	1949-50 Survey	1955-56 Survey		
11	2	5-4	11	45	5-5	11	45	6.74-17.97	12.26	6.82-22.10	11.94	0.00-3.46	1.62	0.03-5.32	1.91	2.52-11.22	7.59	4.31-13.30	7.37	
12	1	4-4	12	4	4-4	12	4	3.07-18.68	13.78	4.39-6.21	5.30	0.00-7.36	1.32	0.00-6.71	1.60	3.34-24.12	9.14	0.00-14.73	7.90	
14	1	4-4	14	4	4-4	14	4	5.80-18.48	14.54	6.90-17.02	13.30	0.08-2.68	1.35	0.03-3.62	1.74	3.44-11.10	8.75	5.64-10.32	8.25	
15	4	5.75-3.25	15	9	4.56-7.11	15	9	8.59-12.71	10.96	9.86-16.05	12.29	1.04-2.53	2.03	0.11-3.26	2.24	6.90-11.93	9.11	3.08-10.78	8.25	
16	18	4.28-6.33	16	1	5-5	16	1	1.13-20.56	12.11	3.11-17.01	11.90	0.00-3.24	1.26	0.24-3.41	1.03	3.60-20.53	9.38	4.07-21.48	10.23	
17	1	5-7	17	1	6-6	17	1	2.48-13.58	11.04	6.10-14.97	11.95	0.00-2.02	1.00	0.00-2.58	0.99	6.44-20.20	10.32	6.38-12.64	8.65	
18	60	4.12-8.32	18	45	3.76-8.47	18	45	3.80-16.12	12.62	2.53-15.52	12.89	0.00-2.68	1.01	0.00-3.02	0.94	2.35-18.90	9.07	4.53-12.31	8.12	
19	1	3-8	19	2	6.50-4.50	19	2	7.80-16.22	13.72	10.64-19.60	13.77	0.00-2.05	0.87	0.00-3.02	0.94	6.18-17.60	7.30	6.18-17.60	8.77	
20	151	2.94-10.45	20	76	3.70-8.56	20	76	3.03-15.91	10.43	6.80-17.59	10.92	0.06-4.14	1.00	0.00-1.40	0.52	0.69-20.33	9.97	5.10-14.32	10.37	
21	50	3.60-11.38	21	46	3.63-10.41	21	46	8.59	9.06	0.90	1.44	9.40	10.00	
22	6	5.67-7.67	22	14	5.86-7.71	22	14	6.06	6.43	0.16	0.16	
24	36	4.92-10.28	24	18	6.56-9.94	24	18	6.06	6.43	0.16	0.16	
25	21	5.71-10.00	25	44	5.11-10.00	25	44	8.59	9.06	0.90	1.44	
26	1	6-12	26	16	3.94-11.56	26	16	6.32	6.43	0.16	0.16	
27	23	4.30-11.17	27	57	3.19-11.84	27	57	12.62	12.89	0.87	0.94	
28	5	5.20-15.50	28	27	3.38-11.85	28	27	13.72	13.77	1.46	0.94	
30	26	6.31-15.96	30	53	9.49-12.92	30	53	10.43	10.92	1.00	0.52	
32	1	8-12	32	1	8-12	32	1	8.59	9.06	0.90	1.44	
33	33	33	1	10-18	33	1	6.06	6.43	0.16	0.16	
34	2	8.00-17.00	34	8	10-16	34	8	6.60	6.43	0.16	0.16	
35	1	5-15	35	1	5-20	35	1	10.87	13.89	1.40	0.24	
36	1	8-12	36	32	6.12-15.25	36	32	4.63	10.63	2.07	0.44	
39	6	4.67-9.67	39	6	4.67-9.67	39	6	10.72	10.72	0.00-1.21	0.57	
40	11	3.64-19.45	40	26	4.00-20.62	40	26	9.34	10.72	0.85	0.24	
42	1	6-24	42	2	10.00-19.00	42	2	8.88	6.38	1.02	0.13-0.36	0.72	
45	2	2.50-25.00	45	11	4.55-19.55	45	11	8.50	9.14	1.33	0.11-1.13	0.59	
50	425	4.38-10.72	50	491	4.86-11.42	50	491	12.49	11.83	1.33	0.00-6.71	1.16	
Total			Total			Total														

43.1%, the N-K mixtures a decrease of 29.8%, and the P-K mixtures a decrease of 33.9%. The average magnesium content of the N-P-K mixtures decreased in all regions except the West South Central and the Pacific and that of the P-K mixtures in all regions except the Middle Atlantic (no samples were taken in the Mountain and the Pacific regions in either survey and no samples were taken in the West South Central region in the 1955-56 survey).

The N-P mixtures showed a decrease of 32.2% in the three regions (West South Central, Mountain, and Pacific) represented by samples in both surveys, even though in two of them (West South Central and Pacific) the average magnesium content increased.

The average magnesium content of the mixed fertilizers as determined in the two surveys are compared to similar figures cited by Mehring (8) for earlier years in Table IV. The data indicate substantially no change in the magnesium content of mixed fertilizers since 1910.

Sulfur. Between the two surveys, the average sulfur content of mixed fertilizers decreased in the Mountain (26.2%), the West South Central (17.3%), the East South Central (8.7%), the Middle Atlantic (2.7%), and the East North Central (1.1%) regions, and increased in the South Atlantic (5.9%), the West North Central (5.9%), the New England (9.4%), and the Pacific (46.0%) regions.

The average sulfur content decreased in 13 of the 22 states represented by samples in both surveys. Six of the states that exhibited an increase were located in the three regions along the eastern coast.

The average sulfur content of the N-P-K mixtures decreased 2.8%, the N-P mixtures decreased 20.2%, the P-K mixtures decreased 15.7%, and the N-P mixtures increased 35.1%.

Mehring (9) reported the mean sulfur content of N-P-K mixtures in 1935 as 8.03% in comparison to 8.58 and 8.17%, respectively, found in the 1949-50 and 1955-56 surveys.

Secondary Nutrients. IN RELATION TO NITROGEN GRADE. Data on secondary nutrient contents in relation to the principal nitrogen grades of the mixtures are summarized in Table V. The 0 to 10% N grades, inclusive, represented 97.6 and 96.5% of the samples in the 1949-50 and 1955-56 surveys, respectively. In the interval between the two surveys, the average calcium content decreased in the 0 to 5% N grades and increased in the 6 to 10% grades; the average magnesium content decreased in all grades except the 3 and 8% N grades; and the average sulfur content decreased in all grades.

In both surveys the calcium content decreased as the nitrogen grade increased, the magnesium content increased up to the 6 to 8% N level and then decreased,

and the sulfur content increased in all grades.

IN RELATION TO P_2O_5 GRADE. Data on secondary nutrient contents in relation to the P_2O_5 grades are summarized in Table VI. In the interval between the two surveys the calcium and magnesium contents decreased in most of the grades. The 4, 5, and 6% P_2O_5 grades exhibited increases in both calcium and magnesium contents and the 16, 20, and 24% P_2O_5 grades showed increases in calcium contents. With the exception of the 6 and 7% grades, the sulfur content decreased in P_2O_5 grades below 15% and increased in grades above 15% except for the 20% grade.

In both surveys the magnesium content decreased as the phosphorus grade increased, whereas the calcium content increased up to the 12 to 15% P_2O_5 level and then decreased, and the sulfur content varied irregularly.

IN RELATION TO K_2O GRADE. Data on secondary nutrient contents in relation to the K_2O grades are summarized in Table VII. In the interval between the two surveys magnesium contents decreased in the 0 to 3% and 9 to 18% K_2O mixtures and increased in the other K_2O grades, sulfur contents decreased in the 0 to 8% K_2O grades and increased in the others, and the calcium contents varied irregularly among the K_2O grades.

In both surveys the magnesium content decreased slightly, as K_2O increased; calcium tended to decrease above the 12 to 13% K_2O level; and sulfur was unchanged to the 12 to 13% K_2O level and then decreased.

IN RELATION TO TOTAL PRIMARY NUTRIENT GRADE. The calcium, magnesium, and sulfur contents tended to decrease in relation to an increase in the individual primary nutrients. The average percentages of the secondary nutrients in relation to the total primary nutrient grade are summarized in Table VIII. In general, the changes in individual secondary nutrients tend to parallel each other in the two surveys. With an increase in total primary nutrients, the magnesium tended to decrease slightly; the calcium and sulfur contents increased up to the 19 to 30% total nutrients level and then decreased rapidly.

Ratios of Secondary Nutrients. TO NITROGEN IN RELATION TO NITROGEN GRADES. The ratios of calcium, magnesium, and sulfur to nitrogen decreased with increasing nitrogen grade. The changes tended to parallel each other in the two surveys.

The calcium-nitrogen and magnesium-nitrogen ratios decreased more regularly than the weight percentages of calcium and magnesium decreased with increasing nitrogen grade. The sulfur-nitrogen ratio decreased, whereas weight per cent of sulfur tended to increase as the nitrogen grade increased.

TO P_2O_5 IN RELATION TO P_2O_5 GRADE. Ratios of calcium, magnesium, and sulfur to P_2O_5 tended to decrease with increasing P_2O_5 grade. The calcium- P_2O_5 ratio decreased to the 6 to 7% P_2O_5 grade, increased to the 8 to 11% P_2O_5 level, and then decreased. The magnesium- P_2O_5 ratio decreased regularly over the entire P_2O_5 range, and except for a slight increase at the 10 to 11% P_2O_5 level sulfur also decreased regularly over the full range. Changes tended to parallel each other in both surveys, with the greatest deviations, however, occurring in calcium- P_2O_5 ratios.

The magnesium- P_2O_5 ratios and the weight percentages of magnesium decreased in both surveys with increasing P_2O_5 grade. The calcium- P_2O_5 and sulfur- P_2O_5 ratios decreased with increasing P_2O_5 grade, whereas the calcium content increased over most of the P_2O_5 range and the sulfur content varied irregularly.

Ratios of Secondary Elements. TO K_2O IN RELATION TO K_2O GRADE. The ratios of calcium, magnesium, and sulfur to K_2O decreased in both surveys with increasing K_2O grade. The changes tended to parallel each other.

Changes in the ratios of the secondary elements to K_2O with increasing K_2O grade decreased more regularly than the corresponding changes in the weight percentages of the elements.

TO TOTAL PRIMARY NUTRIENTS IN RELATION TO TOTAL PRIMARY NUTRIENT GRADE. The ratios of secondary elements to total primary nutrients decreased in relation to increasing total primary nutrient grade. The ratio of calcium to total primary nutrients decreased to the 31 to 34% total nutrient level and then remained relatively constant. The ratio of sulfur to total primary nutrients in the 1955-56 survey exhibited a slight increase at the 31 to 34% level and then decreased. In general, changes tended to parallel each other in the two surveys.

In both surveys and with the three secondary nutrients, the decrease in the ratio of the secondary elements to total primary nutrients was more regular than the change in weight percentages of the elements with increasing grade of total primary nutrients.

Discussion

Scholl and coworkers (10, 11) reported that 12,047,379 and 14,529,159 tons of mixed fertilizers were marketed in the United States in 1949-50 and 1955-56, respectively—an increase of 20.6%. Based on the average percentage figures for the secondary nutrients, the calcium, magnesium, and sulfur tonnages are estimated to have increased, during the six-year interval, 14.2, 5.2, and 14.8%, respectively. Even though the average contents of the secondary elements in the mixed fertilizers declined during the six years, these decreases were not enough

to reduce the total tonnage of calcium, magnesium, and sulfur applied in mixed fertilizers.

Acknowledgment

Grateful acknowledgment is made to L. K. Autry, D. G. Sobers, and H. M. Walen for assistance in the analytical determinations.

Literature Cited

(1) Clark, K. G., Gaddy, V. L., Blair,

- A. E., Lundstrom, F. O., *Farm Chem.* **115**, 17 (1952).
(2) Clark, K. G., Hoffman, W. M., *Ibid.*, 21.
(3) Clark, K. G., Hoffman, W. M., Freeman, H. P., *J. AGR. FOOD CHEM.* **8**, 2 (1960).
(4) Clark, K. G., Lamont, T. G., Winkler, R. R., *Ibid.*, **8**, 7 (1960).
(5) Collier, R. E., *Chemist-Analyst* **43**, 41 (1954).
(6) Malmstadt, H. V., Hadjioannou, T. P., *Anal. Chim. Acta* **19**, 563 (1958).

- (7) Mehring, A. L., *Soil Sci.* **65**, 9 (1948).
(8) *Ibid.*, **66**, 147 (1948).
(9) *Ibid.*, **70**, 73 (1950).
(10) Scholl, W., Wallace, H. M., *Com. Fertilizer* **82**, 21 (1951).
(11) Scholl, W., Wallace, H. M., Fox, E. I., Crammatte, F. B., *Ibid.*, **95**, 23 (1957).

Received for review June 2, 1961. Accepted September 15, 1961. Division of Fertilizer and Soil Chemistry, 140th Meeting, ACS, Chicago, Ill., September 1961.

FERTILIZER MATERIALS

Effect of Particle Size on the Granulation of Triple Superphosphate

BOYCE M. OLIVE and
JOHN O. HARDESTY

Soil and Water Conservation
Research Division, U. S.
Department of Agriculture,
Beltsville, Md.

Granulation efficiency of triple superphosphate during ammoniation was best when the initial material had a low proportion (5 to 15%) of coarse (6–20 mesh), a high proportion (65 to 85%) of intermediate (20–65 mesh), and a relatively low proportion (10 to 20%) of fine (–65 mesh) particles. A higher proportion of coarse particles was detrimental to particle growth, and a higher proportion of fines made the material sensitive to slight variations in moisture content. A triple superphosphate with hard, discrete particles granulated more efficiently than one with soft, fragile particles and indicated greater response to changes in initial average particle size. Both the pattern of size distribution and the average size of raw materials are determining factors in granulation efficiency.

CONCERN ABOUT THE PARTICLE SIZE of raw materials used in fertilizer granulation processes is evident in recent technical literature (1, 4, 10, 12, 14, 18, 20). Standardization of the particle size of raw materials and the effects of particle size on granulation efficiency are subjects of current interest to the fertilizer industry (1, 10, 12). Particle-size requirements depend somewhat on the grade of fertilizer being granulated (16–18). Grades low in nitrogen and high in potash, such as 5–20–20 fertilizer, are reported to be difficult to granulate without the use of rather coarse potassium chloride; whereas high nitrogen grades, such as 10–10–10, appear to granulate well with finer potassium chloride (10–12, 16, 18, 20). There are indications that coarse superphosphate may be substituted to some extent for coarse potassium chloride as a granulation aid (16, 18).

As a consequence of industrial granulation experience, three size classes of potassium chloride have become available on the market (20)—granular, coarse, and regular. Granular potassium chloride, frequently used in processes for granulating low-nitrogen grades, is known to improve both the

movement of material through rotary equipment and the yield of on-size product. However, it interferes with uniformity of nutrient distribution in the product (6, 7, 11, 13). Fine potassium chloride, used in the non-slurry process for granulating mixed fertilizers, often fails to be incorporated into the granule and frequently overloads the processing equipment with recycle material composed largely of potassium chloride.

Industrial experience with potassium chloride and experimental use of both potassium chloride and superphosphate in the granulation of mixed fertilizer indicate that each kind or type of solid ingredient may have a particle-size distribution pattern that is optimum for the most efficient granulation of the mixture.

The effects of variations in the initial particle-size distribution pattern and average size of two triple superphosphates on granulation efficiency are reported here.

Properties of Triple Superphosphate

Chemical and physical properties of triple superphosphates A and B are given in Table I. P_2O_5 and moisture were determined by official A.O.A.C.

procedure (2). Free acid was determined by the acetone extraction method (9). Density measurements of three types were conducted on 10- to 20-mesh particles. True density represents the weight per unit volume of the solid and liquid phase components and was determined by helium displacement. Particle density represents the weight per unit volume of the solid and liquid phase components including voids exhibiting pore diameters of less than 100 microns, which is approximately the size of the openings of a 150-mesh sieve. Particle density was determined by mercury displacement. Bulk density represents the weight per unit volume of the solid and liquid components, including pore volumes and voids between particles, and was determined with the use of a glass cylinder, 5.2 cm. in diameter and 20.4 cm. high. The values for pore volume were calculated from the reciprocals of density measurements according to the formulas shown in Table I.

Particle hardness was determined by crushing-strength tests (7), and is represented by the average crushing strength of 100 6- to 8-mesh particles.

The triple superphosphates were quite