Composition of Fertilizer Granules and the Residues Recovered from Soil

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Residual granules from different soils and crops having the same appearance as the original fertilizer had their chemical composition, weight, and specific gravity studied. The granule volume is maintained during the solubilization of nutrients. From 4–7–5 and 4–7.4–3.3 fertilizers, about 70% of the available phosphorus and all nitrogen and potassium left the granules after one crop cycle.

In spite of the general and even enthusiastic acceptance of granular fertilizer, many consumers are questioning the solubility of the granules because, after harvesting certain crops (cotton, potatoes, tomatoes) and during the plowing for the next culture, they usually find granules having the same appearance as the original fertilizer. Many complaints have been received by the granulators relating these "undissolved" granules to failures in the expected harvest. The object of this investigation was to determine how much of the original available N-P-K of the granular fertilizer migrates into the soil during the fertilization cycle.

Many workers have studied the behavior of granular fertilizers in the soil. The published papers deal with the influence of certain factors upon the yield of the harvest. Some of the factors studied were: granule size (*3*), method of application (*4*), water-soluble and insoluble phosphorus contents (*9*), the diffusion velocity of the mineral nutrient constituents and their assimilation by plants (*2*, *5*, *6*), and comparison between the granulated and dry mixed fertilizer (*1*).

Other papers showed what proportion of the applied phosphorus was assimilated (*7*) and the residual effect of phosphorus addition in the crops of subsequent years (*8*). The chemical literature presents varied information that strongly contrasts with the lack of citations on the composition of the "residual granules" from N-P-K granular fertilizer. In some instances consumers sent residual granules to be analyzed by laboratories and a typical result was:

N	Trace
P	6.1%
K	Trace

Through simple reasoning, the user concluded that all the nitrogen and potassium in the original fertilizer—for instance, 4–7.4(total)—5—was soluble, but only 1.3% of the phosphorus (7.4 − 6.1 = 1.3) migrated into the soil, meaning that the fertilizer, as a whole, was not used profitably. In spite of the correctness of the chemical analysis, this interpretation is not correct, as it is based on only the chemical analysis of the original and the residual fertilizer.

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An example will show how the above figures are misleading. For simplicity, assume an original granule weighing 100 mg. The volume of this granule, with a specific gravity of 1.68, is 0.0595 cc. As the fertilizer analysis is 4% N, 7.4% P (total), and 5% K, the granule, as it is applied to the soil, contains

4.0 mg.	N
7.4 mg.	P (total)
5.0 mg.	K

After the harvest, the "same" granule still occupies 0.0595 cc., and its analysis is now N = trace, (P total) = 5.6%, and K = trace. Now the granule's specific gravity is 0.97, and as its volume remains the same, its weight is only 57.7 mg. This means that the granule contains

0.0 mg.	N
3.2 mg.	P (Total)
0.0 mg.	K

with a reduction of 4.2 mg. of phosphorus, corresponding to a 57% diffusion from the granule:

$$\frac{(7.4 - 3.2)100}{7.4} = 57\%$$

Materials

Granular Fertilizers. The fertilizers used in this work were taken from current production. The formulations are given in Table I and the analyses in Table III. The diameters are from 1 to 4 mm.

Table I. Formulation of Fertilizers Used for Experiments

Composition	Fertilizer, Kg. 4–7–5	Fertilizer, Kg. 4–7.4–3.3
Ammonium sulfate	200	200
Superphosphate (11.2% total P, 10.4% available P)	600	580
Ground rock phosphate (16.2% total P)	100	150
Potassium chloride	100	70

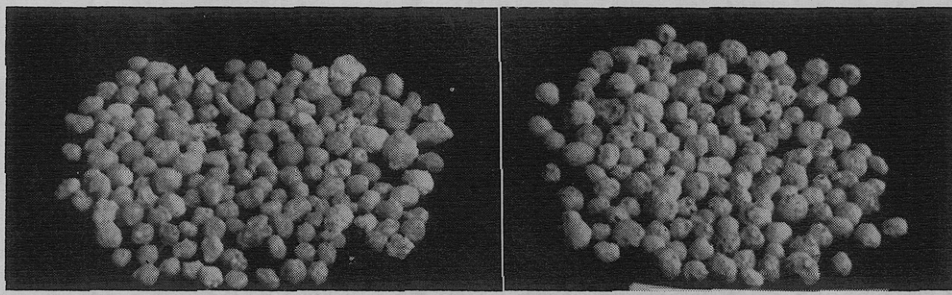

Figure 1. Appearance of original and residual granules after a complete cycle of cotton culture

Left. Original Right. Residual

Granular fertilizers came into general use in Brazil during the past 5 years. At present there are five granulating plants in the state of São Paulo. Since no liquid form of nitrogen is offered at fertilizer prices, all the nitrogen comes in the solid form, mostly from ammonium sulfate and urea. Phosphorus comes generally from straight superphosphate locally produced or from imported triple superphosphate. The raw material for potassium is KCl. To carry out granulation, water or steam is added and the material is dried and cooled. Finely ground phosphate rock is added to give the declared percentage of total phosphorus. Granular fertilizers with N-P-K = 4–7–5 and 4–7.4–3.3 are in current use here.

Residual Granules. These granules were gathered from different regions and crops where the fertilizers were normally used. They resembled the original fertilizer (Figure 1) but were lighter and appreciably softer. A section of a residual granule viewed in the microscope shows a much more porous surface than the original. In laboratory experiments, fertilizer granules conserved their volume and shape after extraction by humid soil and drying (less than 2% volume variation).

Procedure

Chemical analysis was made according to AOAC methods. Available phosphorus is the sum of water-soluble plus neutral ammonium citrate–soluble phosphorus. In the present work, samples of residual granules were picked, one by one, from the fertilized soils.

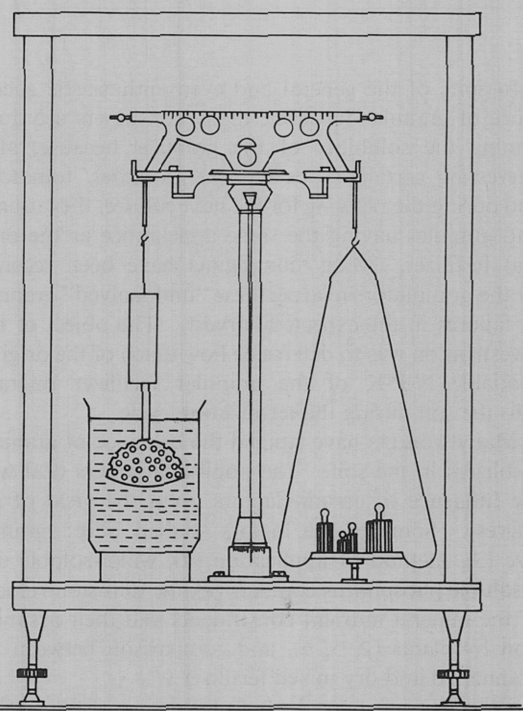

Figure 2. Apparatus for specific gravity determination

Table II. Specific Gravity Determination of a Sample of Residual 4–7–5 Fertilizer

Group	No. of Granules in Group	t_{Hg}, °C.	ρ_{Hg}, G./Ml.	M_o, G.	m, G.	m_o, G.	d, G./Ml.
A	28	23.6	13.5375	1.5104	42.120	25.580	1.13
		23.9	13.5366	1.5071	41.950	25.610	1.14
		24.0	13.5364	1.5056	41.895	25.720	1.15
		24.2	13.5359	1.5038	41.920	25.700	1.15
		24.4	13.5355	1.5022	41.925	25.730	1.15
			Specific gravity 1.15 ± 0.01			Av.	1.15
A	28	23.6	13.5375	1.5104	42.120	25.580	1.13
B	28	24.4	13.5355	1.3918	42.040	26.645	1.12
C	28	24.5	13.5352	1.7692	41.910	23.110	1.16
D	28	24.7	13.5347	1.2876	41.940	27.730	1.13
E	28	24.7	13.5347	1.7653	41.890	22.840	1.15
F	28	24.9	13.5342	1.1469	42.280	29.670	1.13
			Specific gravity 1.14 ± 0.02			Av.	1.14

Table III. Chemical Analysis of Original and Residual Granules

Data	Original Fertilizer[a] 4-7-5	Original Fertilizer[a] 4-7.4-3.3	Residual Fertilizer 4-7-5: 1	2	3	4	Residual Fertilizer 4-7.4-3.3: 5	6	7	8
Regions[b]			Lins	Lins	Araca-tuba	Tupã	Jaú	S.J. Rio Preto	S.J. Rio Preto	S.J. Rio Preto
Crops			Cotton	Cotton	Cotton	Po-tatoes	Cotton	Toma-toes	Toma-toes	Toma-toes
Fertilizer applied, kg. per hectare			330	330	400	1000	400	500	600	600
Months in soil			10	10	9	3	10	$3^1/_2$	4	4
Yield, kg. per hectare			500	200	1200	7:1[c]	1700	8000	8000	10,000
Analysis, %										
N	4.0	4.0	Trace	Trace	0.3	0.2	Trace	0.1	0.1	0.1
Total P	7.4	8.1	5.6	5.5	4.5	4.1	7.2	4.9	6.9	6.2
Available P	5.2	5.3	2.0	2.1	2.0	2.1	2.5	1.9	2.4	2.4
Water-soluble P	4.7	4.8	0.3	0.2	0.2	0.4	0.3	0.3	0.2	0.3
K	5.1	3.8	Trace	Trace	0.7	Trace	Trace	Trace	Trace	Trace
Ca	16.8	17.3	24.6	24.5	21.8	24.5	25.6	25.5	25.4	24.6
S	12.2	12.6	11.2	11.5	12.1	13.4	10.6	11.7	10.7	10.6
Cl	5.1	3.7	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace
Fe	0.3	0.6	0.6	0.6	0.5	—	0.7	—	1.6	1.7
Water (vacuum drying)	2.1	1.5	0.5	0.5	0.2	0.2	0.4	0.4	0.4	0.4
Specific gravity, g. per ml.	1.68	1.65	0.97	1.03	1.17	1.14	1.19	1.10	1.17	1.18
Total residue from 100 parts of original fertilizer			57.7	61.3	69.6	67.9	72.1	66.7	70.9	71.5

[a] Analysis of similar fertilizer with the same formula taken from production.
[b] Regions where fertilizer was applied in São Paulo State (Brazil).
[c] 7 pounds potatoes harvested from 1 pound sown.

Table IV. Comparison of Weights of Constituents in Residual and Original Granules

	Original Fertilizer 4-7-5	Original Fertilizer 4-7.4-3.3	Residual Weights 4-7-5: 1	2	3	4	Residual Weights 4-7.4-3.3: 5	6	7	8
Total residue from 100 parts of original fertilizer	100.0	100.0	57.7	61.3	69.6	67.9	72.1	66.7	70.9	71.5
Nitrogen	4.0	4.0	Trace	Trace	0.2	0.1	Trace	Trace	Trace	Trace
Total P	7.4	8.1	3.3	3.4	3.1	2.8	5.2	3.3	4.9	4.5
Available P	5.2	5.3	1.1	1.3	1.4	1.4	1.8	1.3	1.7	1.7
Water-soluble P	4.7	4.8	0.1	0.1	0.1	0.3	0.3	0.2	0.2	0.2
K	5.1	3.8	Trace	Trace	0.5	Trace	Trace	Trace	Trace	Trace
Ca	16.8	17.3	14.2	15.0	15.1	16.6	18.4	17.0	18.0	17.6
S	12.2	12.6	6.5	7.0	8.4	9.1	7.7	7.8	7.5	7.6
Cl	5.1	3.7	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace

Table V. Reduction of Main Constituents by Dissolution of Fertilizer in Soil

	Samples 1	2	3	4	5	6	7	8
	Reduction, %							
N	100	100	95	97	100	100	100	100
Available P	79	75	73	73	66	76	68	68
K	100	100	90	100	100	100	100	100

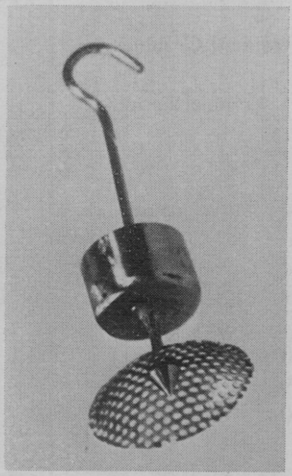

Figure 3. Device for keeping granules under mercury

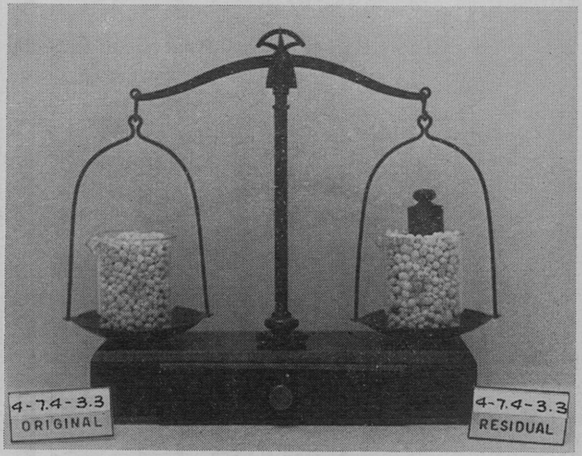

Figure 4. Situation for 4–7.4–3.3 fertilizer

100 grams of original granules = spent granules plus 30 grams of additional weight

From several hundred kilograms of applied granules only a few hundred residual granules were recovered, and no relationship was found between the weight of the fertilizer originally used and the corresponding weight of residue. To calculate a relationship, the specific gravity of the residual granules and of the original granules of corresponding formulas was determined.

Specific Gravity Determination. For the specific gravity determination of granular fertilizer a stainless steel device was used to keep the granules submerged and to measure their loss of weight (Figures 2 and 3). This is, essentially, a cap. A stem connects the cap to a weight at one end; the other end is bent into a hook. The device keeps the granules, which are in the concave part of the cap, submerged in mercury, and hanging on the analytical balance arm, in stable equilibrium. The immersion level is adjusted always at the same level with help of a mark on the stem. The calculation is as follows:

$$d = \frac{M_g \times \rho_{Hg}}{M_g + m - m_o}$$

The precision of the specific gravity determination was tested by repeating it five times with a fixed group of residual granules (Table II), and d = 1.15 ± 0.01 was found. The results (M_g) showed a loss of weight of the granules after each determination and an initial increase of the specific gravity; this can be explained by the opening of pores, accompanied by the erosion of the granules, and caused by their manipulation. The first determination was always taken as the correct one; repeated tests were made to avoid large errors.

The number of granules used for each specific gravity determination was 28. In a given sample of residual granules six different groups of 28 each were tested. The specific gravity obtained was d = 1.14 ± 0.02 with a minimum of d = 1.12 and a maximum of d = 1.16, showing that a group of 28 is large enough to give consistent results (Table II).

Results and Discussion

The chemical analysis and specific gravity determinations made with the original and residual fertilizer are shown in Table III, together with some data about the use of the fertilizers. The last rows show the remaining weight, corresponding to 100 grams of the different formulas used. On the average, fertilizer 4–7–5 left 64 grams, and 4–7.4–3.3 left 70 grams for 100 grams of original material. Figure 4 shows the situation for the second fertilizer. Table IV gives qualitative and quantitative aspects of the composition of the fertilizer granules before and after application to soil. It shows that samples of residual granules from different places and crops are similar in their N-P-K values; the residual fertilizer does not contain water-soluble components of the original fertilizer—nitrogen, potassium, and chlorine were reduced to traces and the remaining water-soluble phosphorus was reduced to only 0.2 to 0.3%; and the original fertilizer contained 5.2 grams of available phosphorus out of 7.4 grams of total phosphorus (70% available), but the residual fertilizer contained only 1.1 grams of available phosphorus out of 3.3 grams total (33% available).

Table V shows that practically all the nitrogen and potassium left the original granules. In the case of phosphorus the reduction was about $^3/_4$. The conclusion drawn is that the "residual granular fertilizer" in spite of its resemblance to the original fertilizer, is composed mostly of insoluble phosphorus and gypsum. The 70% of available phosphorus originally present in the applied fertilizer which passed into the soil is impressive, considering that only 10% of the available phosphorus contained in the fertilizer is generally absorbed by the plants (*7*).

Nomenclature

d = specific gravity, g. per ml.
M_g = mass of the granules, g.
ρ_{Hg} = specific gravity of mercury, g. per ml.
m = mass balancing empty device, g.
m_o = mass balancing device with granules, g.

Literature Cited

(1) Bauw, F. van der, *Chim. Ind. (Paris)* **55,** 369 (1946).
(2) Fontana, P., *Boll. Sci. Fac. Chim. Ind. Bologna* **15,** 103–5 (1957).
(3) Hein, L. B., Hicks, G. C., Silverberg, J., Seatz, L. F., J. Agr. Food Chem. **4,** 318–30 (1956).
(4) Lawton, K., *Atti Simp. Intern. Agro-Chim. 2° Procchio* **1958,** pp. 329–41.
(5) Mitsui, S., Kurihara, K., *Nippon Dojô-hiryogaku Zasshi* **35** (3), 82–6 (1964).
(6) Peterburgskiĭ, A. V., Debreczeni, B., *Isv. Timiryazev. Sel'skokhoz. Akad.,* No. **1,** 76–91 (1961).
(7) Russell, E. J., Russell, E. W., "Las Condiciones del Suelo y el Desarrollo de las Plantas," translation of 8th English ed., pp. 48, 552–3, Aguilar S. A. de Ediciones, Madrid, 1954.
(8) Smith, G. E., *Better Crops Plant Food* **38,** No. 3, 22–30, 40–1 (1954).
(9) Terman, G. L., Anthony, J. L., Mortensen, W. P., Lutz, J. A., Jr., *Soil Sci. Soc. Am. Proc.* **20,** 551–6 (1956).

Received for review April 25, 1966. Accepted September 9, 1966.