

Effect of Superphosphates in
Conserving Nitrogen in Cow
Manure

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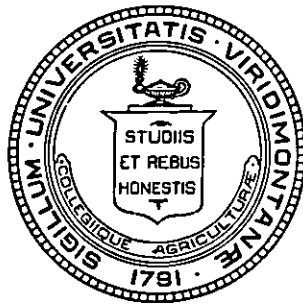
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EFFECT OF SUPERPHOSPHATES IN CON-
SERVING NITROGEN IN COW MANURE

By A. R. MIDGLEY *and* V. L. WEISER



This bulletin discusses the nature and extent of the losses of manurial nitrogen, with special reference to those caused by drying and freezing, as well as the effect of superphosphate usage in lessening these losses. Wastage due to fermentation and leaching is reasonably well understood, but relatively little study has been made of the effects of drying winds or freezing temperatures on manure when spread on the field. Nearly all the available nitrogen may be volatilized as ammonia when fermented manure is exposed to warm drying winds. Freezing losses may also be excessive. However, when superphosphate is mixed with the manure, especially in the gutters where the materials are better able to react, much of the nitrogen which otherwise would be lost is fixed in a somewhat stable form.

Different grades vary in their ability thus to conserve nitrogen, those having a considerable gypsum content outclassing those which contain little of this amendment. Gypsum itself is of slight avail, but is quite serviceable when used in conjunction with a phosphate. Thoroughness of admixture with manure enhances the usefulness of superphosphate and it is much better to apply it before rather than after fermentation.

Since almost all Vermont soils contain inadequate supplies of available phosphorus, the use of this amendment in this fashion serves a double purpose, preventing a wastage of one form of plant food and supplying another which is relatively lacking.

BULLETIN 419: EFFECT OF SUPERPHOSPHATES IN CONSERVING NITROGEN IN COW MANURE

A. R. MIDGLEY and V. L. WEISER¹

Commercial nitrogen is much less costly now than it was several years ago yet, notwithstanding, the dairy farmer can well afford to conserve manurial nitrogen. It is poor practice to let it escape from the farm and then spend money to replace the loss.

The importance of conserving manure can hardly be overstated. More than 4,000,000 tons are produced annually in the small State of Vermont. Its crop-producing value at Slipher's (24) estimate—\$2.50 a ton—is \$10,000,000. It is a very perishable product. It has long been known that material losses, especially of nitrogen, occur between the stable and the soil. The purpose of this study has been to determine the magnitude of some of these losses, their causes, and the effect of admixing superphosphate with the manure as a means of reducing them, especially while the mass is fermenting and, later, subjected to drying and freezing conditions.

REVIEW OF LITERATURE ON EFFECT OF CHEMICAL AMENDMENTS

The preservation of manurial nitrogen by the use of chemicals has been studied by many workers. The materials may either act as disinfectants, inhibiting the formation of ammonia, or form stable salts with ammonia after it has been produced, thus preventing its loss by volatilization.

Many antiseptics have been used: carbon bisulphide by Aeby, et al. (1); chloroform, bleaching powder and formalin by Berry (4); zinc chloride, copper sulphate and formalin by Lemmerman and Wiessmann (17). Gerlack (9) and Joshi (15) found that formaldehyde lessened the loss of urinary nitrogen compounds as did also Blank (6), who claims that manure so treated decreases crop yields. In general it can be said that preservatives of this type are effective in reducing nitrogen losses if added in amounts sufficient to prevent microbiological activity, but that they are worthless under practical conditions because of cost and sundry undesirable characteristics.

The chemical preservatives which form non-volatile ammonium salts are mainly mineral acids and acid salts. Nolte (22) found such acid salts to be reasonably effective in conserving nitrogen, whereas salts of such strong alkalis as sodium and potassium were of little value.

¹ The writers acknowledge the assistance of E. L. Mayton, M.S., former research fellow.

Mineral acids, especially phosphoric and sulphuric, have been often used with fairly good results. Lindsey (19), Immendorf (14), and Wisselink (30) found sulphuric acid to be efficient but impracticable for use under farm conditions.

Gypsum (land plaster) has been tried by many investigators with varying outcomes. Vivien (27), Heinrich (12), Severin (23), and Gerlack (9) report good results, whereas Nolte (22), Collison and Conn (8), Muntz and Girard (21), and Immendorf (14) deem it to be of no value. Bear and Workman (3), using pure ammonium carbonate and calcium sulphate, secured a double decomposition, ammonium sulphate and calcium carbonate being formed, and concluded that gypsum might fix ammonia if the water content of the manure were sufficiently high.

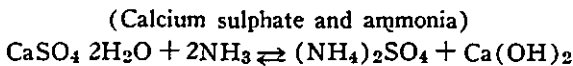
Superphosphate has received more attention than any other similar amendment. Very few workers have decried its use. Meyer (20) reduced the drying losses of ammonia in liquid manure 27 to 100 percent. Björn-anderson (5) found that two percent of superphosphate added to liquid manure reduced while four percent prevented all ammoniacal losses. Gerlack (9) says that it is the best known preservative of urinary nitrogen and states that no loss whatsoever occurs when it is used in amounts sufficient to impart a permanent slightly acid reaction. Collison and Conn (8) reduced the nitrogen loss in manure 15 to 51 percent and lessened that of organic matter. Other workers, such as Immendorf (14) and Slipher (24), secured similar results.

HOW SUPERPHOSPHATE CONSERVES NITROGEN IN MANURE

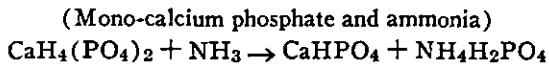
Before considering the way in which superphosphate acts in conserving manurial nitrogen, it may be well to review the composition of manure and the changes which it undergoes.¹ It has long been known that the nitrogen content of cattle manure is affected by feed, kind and age of animal, season of the year, amount and kind of bedding, etc. Cattle excrement is made up of about 70 parts solid and 30 parts liquid by weight. The nitrogen content of the dung varies from 0.2 to 0.45 percent, averaging between 0.35 and 0.40 percent (seven to eight pounds per ton); that of the urine from 0.8 or less to over 1.5 percent, averaging about 0.95 percent (19 pounds per ton). When the complete excrement is mixed with enough straw as bedding to absorb the liquid, the mass contains about 0.5 to 0.6 percent of nitrogen, half of it derived from the urine. If it stands for a few days, much of the urinary nitrogen is converted into ammonia. Thus manure containing 10 to 12 pounds

of nitrogen per ton will carry nearly half of its nitrogen in the form of ammonia. Since the urine is the more valuable portion, such mechanical losses as seepage and run-off should be prevented as well as those due to this chemical change. Urea is readily converted into ammonium carbonate which is very volatile, especially when the manure dries. It is in preventing this loss that superphosphate plays its greatest rôle.

Superphosphate consists mainly of calcium sulphate (gypsum) and mono-calcium phosphate. The former is relatively ineffective when used alone for, even if ammonium sulphate does form, the remaining basic calcium compound is apt to drive off ammonia, especially if the mass dries.

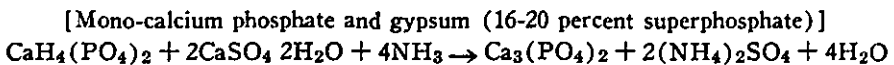


On the other hand, mono-calcium phosphate can hold some ammonia, for it readily reacts to form mono-ammonium and di-calcium phosphates. The latter is not sufficiently basic to expel ammonia even when the manure dries out. However, it is inefficient, since only a part of the hydrogen is replaced by ammonia, as seen in the following equation:



While it is possible to replace one more hydrogen with the formation of di-ammonium phosphate, yet tri-ammonium phosphate can not be formed since it is very unstable and readily breaks up, releasing ammonia gas.

When a mixture of mono-calcium phosphate and gypsum (such as a 16 or 20 percent superphosphate) is used in the presence of ammonia, these ingredients become much more effective per unit of phosphate present, as can be readily seen in the following reaction:



Clearly the acid of the original phosphate is completely neutralized in the formation of tri-calcium phosphate and, since the calcium is removed, an equivalent amount of sulphate remains to form ammonium sulphate. Since sulphuric acid combines to better advantage with ammonia than phosphoric acid, the latter has often been found to be less effective when added to manure than sulphuric acid of the same strength. It is difficult to replace all of the hydrogen in phosphoric acid with ammonia, whereas all of that in sulphuric acid is easily replaced.

An excess of ammonium carbonate was added to standard sulphuric and phosphoric acids, the mixtures dried at room temperature with a fan,

and the amount of residual ammonia determined in each case. The phosphoric acid held only half as much ammonia as did sulphuric acid of a similar strength. However, when calcium sulphate was added to these acids and the masses similarly dried, the phosphoric held practically as much ammonia as did the sulphuric acid mixture, the calcium precipitating as tri-calcium phosphate, thus leaving an equivalent amount of sulphuric acid to form ammonium sulphate. These facts explain why calcium salts in conjunction with phosphates are so effective in holding ammonia.¹

SUPERPHOSPHATE AS A MEANS OF REDUCING FERMENTATION LOSSES

Storage losses of manurial nitrogen seem to have received more attention than other forms of wastage. Cow manure is a so-called "cold manure," yet it loses nitrogen during ammonification and fermentation. The first step, ammonification, occurs promptly, most of the urea changing to ammonium carbonate within a few days. During the next stage, fermentation, volatile organic acids are formed which hold part of the ammonia as their salts. During ammonification, the pH rapidly increases to about pH 8 or 9, but when fermentation takes place, especially if enough moisture is present and air is more or less excluded, it decreases to some extent.

TABLE 1.—EFFECT OF 16 PERCENT SUPERPHOSPHATE UPON FERMENTATION LOSSES OF NITROGEN FROM COW FECES AND URINE SEPARATELY AND WHEN MIXED TOGETHER

Treatment—Pounds per ton of manure	Pounds of nitrogen in 10 tons of material				Percentage nitrogen lost in 3 months
	At beginning	After 1 month	After 2 months	After 3 months	
Feces	77.4	78.	73.8	72.	7.
Feces + 40 pounds 16 percent superphosphate per ton....	77.4	78.4	79.2	73.8	4.9
Feces + 80 pounds 16 percent superphosphate per ton...	77.4	78.4	79.	78.	No loss
Urine	129.4	47.8	20.6	14.	89.2
Urine + 40 pounds 16 percent superphosphate per ton....	129.4	128.4	55.6	38.	70.6
Urine + 80 pounds 16 percent superphosphate per ton....	129.4	129.2	92.	72.2	44.2
Urine + feces	117.4	95.2	84.6	68.2	41.9
Urine + feces with 40 pounds 16 percent superphosphate per ton	115.	103.4	89.	76.	33.9
Urine + feces with 80 pounds 16 percent superphosphate per ton	112.8	103.6	93.2	85.	24.7

¹ For a more detailed study on the ammoniation of superphosphate see Keenan (16) and White, Hardesty, and Ross (29).

Theoretically daily haulage and spreading are desirable, but it is rarely possible to do this, and storage becomes necessary. In order to determine the extent of these fermentation losses, dung and urine were collected and used separately and mixed together, 1,000-gram portions being weighed into one-gallon crock jars and the amendment thoroughly incorporated. The jars and their contents were stored at room temperature, original moisture percentages being maintained by additions of distilled water. The materials were sampled and analyzed at the beginning and at one-, two-, and three-month intervals (table 1).

Obviously superphosphate always worked well as a preservative, the higher rate of application proving superior. It was most effective when used on urine alone, conserving over 58 pounds of elemental nitrogen in a normal 10-ton application. The total nitrogen loss from fecal fermentation was much less than that when urine was fermented, as was to be expected since its nitrogen is in a much more resistant form.

SUPERPHOSPHATE AS A MEANS OF REDUCING DRYING LOSSES

Drying losses often exceed all others. When manure is spread on the field considerable loss of moisture occurs, its magnitude depending on weather conditions and the time elapsing before incorporation into the soil. Manure is often hauled out in the spring during corn planting time and, if it is not promptly covered, the warm drying winds may volatilize practically all the available nitrogen. Considerable loss may also result when it is applied as a top-dressing on meadows or pastures, especially if it dries before the rains wash it into the soil.

A review of literature shows that few workers have studied the nature and extent of this wastage, whereas many have investigated those of fermentation losses. Heck (10, 11) has shown that this loss falls on the most available portion of the manurial nitrogen and, together with fermentation losses, may amount to 50 percent of the total. He obtained the greatest drying loss with manure that was ammonified but not completely fermented, the next greatest with that which had fermented. He also found that its extent depended on weather conditions, dry, windy weather augmenting losses which are lessened if rain occurs before drying.

Björn-anderson (5) states that losses of urinary nitrogen can be avoided during storage but that wastage by drying after spreading is very hard to overcome. However, the addition of two percent of superphosphate to the urine appreciably reduced the drying loss, while all of it could be controlled when four percent was used.

Meyer (20), drying well-ammonified urine at room temperature, obtained almost complete loss of nitrogen but when sulphuric acid was added in amounts equivalent to the quantity of ammonium carbonate present, only two percent escaped. Phosphoric acid, superphosphate, and gypsum used in similar quantities were less effective.

Large drying losses may occur with comparatively fresh manure. Ames and Gaither (2) report that 30.6 percent of the nitrogen escaped from comparatively fresh cow manure which had been air-dried at a temperature of 60° C., due no doubt to loss of ammonia. Muntz and Girard (21) state that appreciable quantities of ammonia are formed in a few hours at temperatures ranging from 2° C. to 30° C. Waksman and Diehm (28) point out that urinary nitrogen may all be converted into ammonia in 48 hours.

Most dairy barns are quite warm during much of the year and the gutters highly inoculated with ammonifying organisms. This is why much ammonia may be produced in a very short time. Even though manure is moved from the stable daily and spread at once, it may still suffer considerable loss by drying. Freshly voided cow manure contains very little, if any, ammoniacal nitrogen; yet 24-hour-old manure collected from cows at this Station contained large quantities which were readily lost upon drying.

Since many dairymen remove manure once or twice daily and pile it under outdoor conditions, the question arises as to the extent of fermentation and subsequent drying losses that may occur at different seasons of the year. Three 500-gram lots of fresh cow manure were placed in suitable containers and maintained at three different temperatures for one month. The jars were supplied with loose-fitting covers which allowed the gases to escape. Initial moisture contents were maintained by the addition of distilled water at regular intervals. Duplicate samples were taken and analyzed at the beginning and at the end of the one-month period to determine fermentation and subsequent drying losses when dried with a fan at room temperature (table 2).

TABLE 2.—EFFECT OF DIFFERENT TEMPERATURES ON FERMENTATION AND SUBSEQUENT DRYING LOSSES OF WHOLE COW MANURE (FERMENTED ONE MONTH)

Temperatures held during fermentation	Pounds of nitrogen lost in 10 tons of manure		
	Lost during fermentation	Lost when dried	Total lost through fermentation and drying
Cool—12-15° C.	2.	51.7	53.7
Warm—30-33° C.	9.2	39.3	48.5
Hot—50-51° C.	17.1	34.1	51.2

Fermentation losses were small when the manure was held at low temperatures, but became greater as these rose. Obviously much ammonia was produced at the cool temperature because the loss was excessive when the manure was dried. In fact, the total loss by fermentation and drying was greater at the low than at the higher temperatures. Microbiological activity is augmented in warm and hot weather and the organisms store large quantities of nitrogen in their own structures. The losses were very great; in fact, only about one-half of the total nitrogen content remained after fermentation and drying, if one assumes that there are about 100 pounds originally present in 10 tons of manure. It is evident that great care should be used to prevent drying, even though the excreta are stored at low temperatures (winter).

The higher the temperature at which manure is held the greater the fermentation loss. Borings made into several manure heaps in the early spring showed that temperature never exceeded 15° C. Under such conditions fermentation losses are few, but they may become much greater if the manure is later allowed to dry.

It is almost impossible entirely to prevent this drying loss, but superphosphate has been found to be very helpful in inhibiting it, as is indicated in tables 2, 3, 7, 9, and 10.

SUPERPHOSPHATE AS A MEANS OF REDUCING FREEZING LOSSES

Losses of nitrogen from manure by freezing are much the same in amount, though not in nature, as those due to drying. The latter are brought about by the vaporization of water from manure and the consequent concentration of the ammonia in solution until, finally, that which is not held in combination with some stable compound is itself volatilized. In freezing weather the water is removed by crystallization. The moisture in the former case is changed to a gas, while in the latter it is changed to a solid. The results are much the same in either case, except that freezing losses are not so large. Liechti and Ritter (18) report that one-third of its ammonia may be lost when manure is spread on the snow.

In order to determine the extent of these losses, one-month-old fermented cow manure was used so as to have a material high in ammoniacal nitrogen and because most manure is more or less fermented before it is piled or spread on the land and allowed to freeze. Duplicate 50-gram samples, with and without superphosphate, were frozen under outdoor conditions for 48 hours at approximately 23° F. (—5° C.), and their

ammoniacal nitrogen contents as well as those of a similar unfrozen sample were ascertained (table 3).

TABLE 3.—EFFECT OF FREEZING ON LOSSES OF MANURIAL NITROGEN (ONE-MONTH-OLD FERMENTED MANURE SUBJECTED TO 23° C. FOR 48 HOURS)

Treatment	Ammonia remaining in 50 g of manure	Nitrogen remaining in 10 tons of manure
	mg.	lb.
Manure, unfrozen	119.	48.
Manure, frozen	63.	25.
Manure + superphosphate, frozen*	73.5	29.4

The losses due to freezing are much the same as those due to drying but are usually less severe; however, one-half of the total ammoniacal nitrogen may be thus wasted. Superphosphate reduces this loss, but it is less effective than one might suppose it to be since it has been added to fermented manure containing considerable ammonium carbonate (see page 14, table 8).

Even greater losses occurred in another trial in which the manure was exposed to freezing. Much moisture was evaporated; hence, all the loss can not be attributed to freezing alone.

SUPERPHOSPHATES AS A MEANS OF CONSERVING MANURIAL NITROGEN

Many dairymen use superphosphate in their stables during the winter to balance and conserve their farm manure supplies. Superphosphates containing more than 16 percent available phosphoric acid are now made and sold. The question arises how higher-analysis goods—the 20 and 40 percent grades—compare with the 16 percent material for this purpose.

Four superphosphates, 16 percent pulverized, 20 percent both pulverized and granulated, and 40 percent granulated, were used. They differ decidedly in their calcium sulphate contents, moisture percentages, and acidity (table 4).

TABLE 4.—CHARACTERISTIC DIFFERENCES BETWEEN FOUR SUPERPHOSPHATES

Type	Gypsum	Moisture	Acidity
	Percent	Percent	pH
20 percent granular	60	1.	3.05
20 percent pulverized	58	1.5	3.45
16 percent pulverized	54	5.8	3.55
40 percent granular	3-4	3.6	2.75

* 1.25 grams of 20 percent superphosphate and 50 grams of fermented manure; equivalent to 50 pounds per ton of manure.

The 20 percent granulated goods contain more gypsum than do the other materials, partly because they are drier, much of the hygroscopic water as well as the water of crystallization having been removed in the granulation process. Run-of-pile goods now made often contain 20 percent P_2O_5 and filler is frequently used to make it grade 16 percent, sand, and sometimes lime, being added. This may account for the somewhat lower calcium sulphate content in the 16 percent grade. Their several degrees of acidity are much the same, the granulated being slightly more acid than the pulverized grades. This statement holds especially for the 40 percent granulated goods, the increases being perhaps due to the presence of a little relatively free phosphoric acid.

Much research has been carried on with these materials to determine their ammonia-holding capacities. The results in general show that when compared on the same P_2O_5 basis, their ammonia-holding capacities are proportionate to their calcium sulphate contents. That is to say, one gram of 40 percent superphosphate will hold more ammonia than one gram of 20 percent superphosphate, but not nearly twice as much. The addition of gypsum to superphosphates low therein greatly increases their efficiency, as is evidenced by the results secured in the following trial. One-gram portions of 20 and 40 percent superphosphates and mono-calcium phosphate containing 52.3 percent P_2O_5 were placed in beakers and amounts of gypsum increasing from 0.25 to 2 grams added to each. They were then drenched with an excess of dilute ammonium hydroxide, allowed to react, dried with a fan at room temperature, and their ammonia contents determined (table 5).

TABLE 5.—EFFECT OF ADDING GYPSUM TO 20 AND 40 PERCENT SUPERPHOSPHATES AND TO PURE MONO-CALCIUM PHOSPHATE, ON THEIR AMMONIA-HOLDING CAPACITIES

Gypsum added	Percentage nitrogen held per gram of		
	20% superphosphate	40% superphosphate	Mono-calcium phosphate
No gypsum	5.	6.82	7.71
0.25 g gypsum	5.85	8.80	12.13
0.5 g gypsum	5.89	11.57	14.27
0.75 g gypsum	5.91	13.39	16.47
1. g gypsum	5.89	14.16	18.23
1.5 g gypsum*	20.7
2. g gypsum	22.1

1. g of gypsum with superphosphate only held 0.15 percent nitrogen.

The ammonia-holding capacities of both 40 percent superphosphate and mono-calcium phosphate were greatly enhanced by additions of gypsum, while that of the 20 percent material was not significantly

* Not determined.

altered. The latter normally contains about 58 percent gypsum, while the 40 percent material carries only small amounts and the mono-calcium phosphate none. Its value as a supplement is well illustrated, since when used alone it conserves very little ammonia. It is also obvious that without gypsum a unit of either mono-calcium phosphate or 40 percent superphosphate holds more ammonia than does one of 20 percent superphosphate. However, on the basis of their comparative phosphorus contents the mono-calcium phosphate should hold nearly thrice and the 40 percent twice as much as the 20 percent material, which does not occur until considerable gypsum has been added. The small gypsum content of 40 percent superphosphate accounts for the greater efficiency of its P_2O_5 content when compared with mono-calcium phosphate at the beginning. This is apparent since 40 percent superphosphate fixed 6.8 percent, while 56.3 percent mono-calcium fixed only 7.7 percent nitrogen, whereas on the same P_2O_5 basis the latter should have fixed 9.5 percent.

The conservation of liquid manure is always a problem on a dairy farm, especially where bedding material is scarce; hence, the relative urine- or water-holding capacities of these four superphosphates were studied in the manner suggested by Hilgard (13) (table 6).

TABLE 6.—RELATIVE WATER-HOLDING CAPACITIES OF FOUR SUPERPHOSPHATES (100-GRAM BASIS)

Superphosphate used	Total water held	Original moisture present	Net water-absorbing capacity
	g	g	%
16 percent pulverized	78.5	5.8	72.7
20 percent pulverized	61.7	1.5	60.2
40 percent granulated	49.1	3.6	45.5
20 percent granulated	30.2	1.	29.2

The pulverized material holds water better than does the granulated. It absorbs more liquid but does so much more slowly. It is hard to understand why the 20 percent granulated is not more efficient since its initial moisture content is less than that of the other materials. Possibly less surface area is actually exposed for absorbing liquid. If these comparisons were made on a volume basis, the 20 percent granulated superphosphate would rate somewhat higher, being heavier and having a greater specific gravity, but in practice it is bought and used on a weight basis. However, only a little is normally used in the dairy barn and it is really a rather small item to consider. This disadvantage is partly overcome by the fact that the stable walks are less slippery and less dusty when the granular replaces the pulverized form.

The relative ammonia-conserving powers of these four superphosphates and phosphoric acid, when added to fermented manure and then dried, were also studied. Eight 50-gram samples of well-fermented whole manure, containing about one-half of its total nitrogen in the form of ammonium carbonate, were weighed into small beakers and handled in duplicate. In order to determine the total amount of ammonia present one set was not dried; the others were dried after treatment with or without phosphatic materials. One lot of 20 percent granulated superphosphate was first pulverized (40-mesh) in order to see whether it would be more effective in that condition. Since 40 percent superphosphate contains twice as much P_2O_5 as the 20 percent material, only one-half as much was used (table 7).

TABLE 7.—RELATIVE CAPACITIES OF FOUR SUPERPHOSPHATES AND PHOSPHORIC ACID TO CONSERVE AMMONIA WHEN THOROUGHLY MIXED WITH FERMENTED MANURE

Treatments and phosphates used	Pounds per ton of manure	Ammonia as nitrogen in 10 tons of manure after treatment	
		Total ammonia nitrogen	Percentage recovered by treatment
		lb.	%
Manure, not dried	52.	100.
Manure, dried	3.8	7.3
Manure + 16 percent pulverized superphosphate, dried	50	16.4	31.5
Manure + 20 percent pulverized superphosphate, dried	50	17.6	33.8
Manure + 20 percent granular superphosphate, dried	50	16.	30.8
Manure + 20 percent granular superphosphate (pulverized), dried ...	50	18.5	35.6
Manure + 40 percent granular superphosphate, dried	25	11.7	22.4
Manure + phosphoric acid, dried....	Eq.*	26.5	51.

Very large losses ensued, but they were lessened when the amendments were used. The granular materials were less effective, and perhaps less active, than the pulverized, being apparently unable to react so completely, as is evident when one compares the ammonia-holding capacity of the 20 percent goods in the granular form with that of the same material when pulverized, in which state it held more ammonia than did any other superphosphate used.

Phosphoric acid was more effective than any other phosphatic material, being in a very active form and without a base. A high ammonium carbonate content in manure does not greatly affect the efficiency of phosphoric acid, but it does reduce the capacity of superphosphate to hold ammonia. (See page 14.)

* H_3PO_4 used to supply P_2O_5 equivalent to 20 percent superphosphate.

LIMITATIONS OF SUPERPHOSPHATE IN CONSERVING MANURIAL
NITROGEN

Superphosphate aids materially in reducing nitrogen losses of manure, especially those due to drying, but it is less effective than one might expect, considered from a purely chemical standpoint (table 8).

Ammonium hydroxide, carbonate, hydrosulphide, and polysulphide were chosen by the writers because conceivably all of them may form during the fermentation of manure. In fact, preliminary trials had shown that fermented manure contains large quantities of carbonates and sulphides, the latter presumably produced from sulphates and other sulphur-containing materials under reduction conditions. Indeed, it is quite possible that the foul odor of stored manure is due to volatile ammonium sulphide.

Six lots of 16 percent superphosphate of 2.5 grams each were exposed to sundry ammoniacal vapors and to fermented manure. They were weighed into small flasks, each containing 10 cc of distilled water. Air was bubbled through each superphosphate suspension after it had absorbed volatile gas from the chemical or the manure, as the case might be. Bromthymol blue indicator was added to each suspension and the ammonia-laden air bubbled through it until it became distinctly basic in its reaction. The superphosphate mixtures as well as the manure and superphosphate were all dried at room temperature with a fan, after which the amount of remaining ammonia was determined (table 8).

TABLE 8.—EFFECT OF DIFFERENT AMMONIUM COMPOUNDS ON THE CAPACITY OF
2.5 GRAMS OF 16 PERCENT SUPERPHOSPHATE TO HOLD AMMONIA

Source of ammonia used	Ammoniacal nitrogen recovered after treating and drying 2.5 g superphosphate
	mg.
Ammonium hydroxide	94.5
Ammonium hydrosulphide	74.2
Ammonium carbonate	59.5
Ammonium polysulphide	58.8
Gas from 50 g of fermented manure*	75.5
50 g of fermented manure (superphosphate and manure inter- mingled)	38.5

According to the gases used, superphosphate varied in its capacity to hold ammonia after drying. It was most effective with ammonium hydroxide, while gases derived from fermented manure were next. The poorest results were secured when superphosphate was added directly to manure, the amendment being less than one-half as effective as it

* The fermented manure was heated and partly dried in order to get sufficiency of ammonium gases.

was in the former case. This fact is significant when one realizes that the manure itself holds some ammonia when similarly dried.

Much laboratory work has shown that superphosphate holds less ammonia when added to manure than when brought in contact with its gases. In other words, its efficiency is impaired by such contact. Manure is so viscous that superphosphate is seldom able to react with it completely (see data on intimacy and time of contact in table 9). Furthermore, it is quite possible that micro-organisms consume much of the applied phosphorus, as suggested by Tottingham and Hoffman (25, 26). While they also consume nitrogen, it is questionable whether the proportion of nitrogen to phosphorus thus held would be the same as that held chemically if the superphosphate were not used by organisms. Thus, the efficiency of superphosphate may or may not be decreased in this manner.

During the decomposition of manurial proteins amino acids are necessarily produced. Some of these, as well as urea, have basic properties and may react with the superphosphate and thus reduce its efficiency in holding ammonia. Since they are usually stable they are not lost during drying, whether the manure is or is not treated with superphosphate. By replacing ammonia in this fashion, more volatile ammonia would escape; in other words, when present, they interfere with or reduce the power of superphosphate to hold ammonia.

Another reason why this amendment is more effective is that a large amount of ammonium carbonate is present, especially in ammonified or fermented manure. When superphosphate is added to ammonium carbonate much calcium carbonate is formed. When this salt, together with ammonium sulphate, is dried, ammonia is volatilized and lost as carbonate. When no carbonate is present, more of the calcium is precipitated as tri-calcium phosphate and the more stable and resultant ammonium sulphate remains. It should be remembered that superphosphate is most effective in holding ammonia when most or all of the phosphorus is converted into the tri-calcium phosphate form, since the calcium is removed from calcium sulphate and leaves an equivalent amount of acid radical to form ammonium sulphate. Hence it can be seen that superphosphate treated with ammonium hydroxide holds more ammonia when dried than when treated with ammonium carbonate.

HOW SUPERPHOSPHATE SHOULD BE USED WITH MANURE

To be most effective, superphosphate should be intimately mixed with fresh manure. It is best to use it in the stable gutters, which should

be water tight in order that urine and phosphorus may not be lost through leachage. Some should be spread on the walks—for appearance and sanitation—but most of it should be placed in the gutter where the best opportunity is afforded for the urine to dissolve and react with the superphosphate.

The influence of time and intimacy of contact between superphosphate and fermented manure in preventing drying losses was studied. Fifty-gram portions of one-month-old fermented manure were placed in beakers and treated with 20 percent pulverized superphosphate at rates equivalent to 50 and 100 pounds per ton of manure (1.25 and 2.5 grams, respectively). The contents of the beakers were treated with chloroform to inhibit micro-organic activities so that the composition of the manure might remain constant during the drying process. One set was dried promptly after partial mixing in the phosphate, the second was stirred thoroughly and repeatedly while drying, and the third received extra water to make it less viscous and facilitate mixing. The latter was then left for three days before it was dried, during which time it was occasionally stirred. Drying was accomplished at room temperature with a current of air from an electric fan. The amount of ammonia remaining in each lot after drying was determined (table 9).

TABLE 9.—EFFECT OF TIME AND INTIMACY OF CONTACT BETWEEN SUPERPHOSPHATE AND FERMENTED MANURE IN PREVENTING DRYING LOSSES OF AMMONIA

Degree of mixing superphosphate with manure before drying	Pounds of ammonia as nitrogen remaining in 10 tons of dried manure when treated with superphosphate	
	50 lb. per ton of manure	100 lb. per ton of manure
Partially mixed, then dried	8.4	11.
More completely mixed, then dried	11.	15.6
Thoroughly mixed, then dried	16.8	27.6

The more thorough the mixing process, the more efficient was the amendment, whether more or less superphosphate was used. Ammonia retention was augmented not only by thorough mixing but also by the allowance of more time for reaction before drying. The maximum reaction attained with 50-pound usage was much more efficient than when 100 pounds were applied and partially mixed before drying.

Preliminary trials have indicated that superphosphate is less effective in preventing drying losses when added to manure after fermentation than when it is present in the manure during fermentation. To obtain additional information, whole, fresh manure was thoroughly mixed and four 50-gram portions weighed in duplicate, placed in small beakers

with glass covers, and stored at room temperature for two weeks, the moisture contents being kept constant by the addition of distilled water at regular intervals. Superphosphate was mixed with the manure at the outset—before fermentation—in one set, with the manure after fermentation in another, while the third was left untreated. All sets except one were dried with an electric fan at room temperature in order to determine drying losses and the effect of adding superphosphate before or after fermentation on these losses. The amounts of ammoniacal nitrogen remaining in the manure after such treatments are presented in table 10, together with maize yields when fertilized with such manures.

Crop-producing values were determined by adding 100-gram portions of fresh manure treated in the manners above indicated to a very sandy soil contained in two-gallon crop jars (10 tons of manure per acre basis). One jar was left unmanured, while to another were added nitrogen, phosphorus, and potassium as inorganic salts equivalent to the total material present in the fermented, undried manure. In order that similar amounts of phosphorus might be present for plant growth, superphosphate was added to each jar before seeding, either to the manure as specified or directly to the soil.

TABLE 10.—EFFECT OF ADDING 20 PERCENT SUPERPHOSPHATE TO MANURE BEFORE OR AFTER FERMENTATION ON CONSERVATION OF AMMONIA AND MAIZE YIELDS FROM AN APPLICATION OF 10 TONS OF TREATED MANURE PER ACRE BASIS

Treatment	Ammonia recovered in	
	10 tons of manure	Corn yields 2 harvests
	lb.	g
Check—no manure	0	15
Manure fermented, not dried	45.3	192
Manure fermented and dried	3.5	35
Manure, superphosphate used before fermentation, dried	32.	152
Manure, superphosphate used after fermentation, dried...	10.2	46
Nitrogen, phosphate, and potash (no manure)	248

Clearly, it is much better to add superphosphate to manure before fermentation than after. The former procedure saves over three times as much ammonia as the latter and produces three times as great a crop. Part of this great difference may be ascribed to fermentation losses when no amendment is used, although during this brief period such losses are slight, especially when the high original moisture content is maintained.

An intimate admixture of amendment and manure and a relatively long period of reaction are important because of the low solubility of superphosphate. If added to manure before it ferments, the phosphate

is better able to hold nitrogen than when used on the pile or load as it is being spread on the land and subjected to drying conditions.

Fermented manure also contains much ammonium carbonate, which reduces the capacity of superphosphate to hold ammonia when subsequently dried (page 14). Fresh manure contains practically none and facilitates the solution and reaction of the superphosphate before the carbonate is produced.

Fermented manure treated with superphosphate holds about three times as much ammonia as it does without it, although the efficiency of the superphosphate is somewhat lessened when used in this way. However, it is doubtful whether the two are ever mixed as thoroughly in practice as in these trials, and whether much ammonia is saved when the

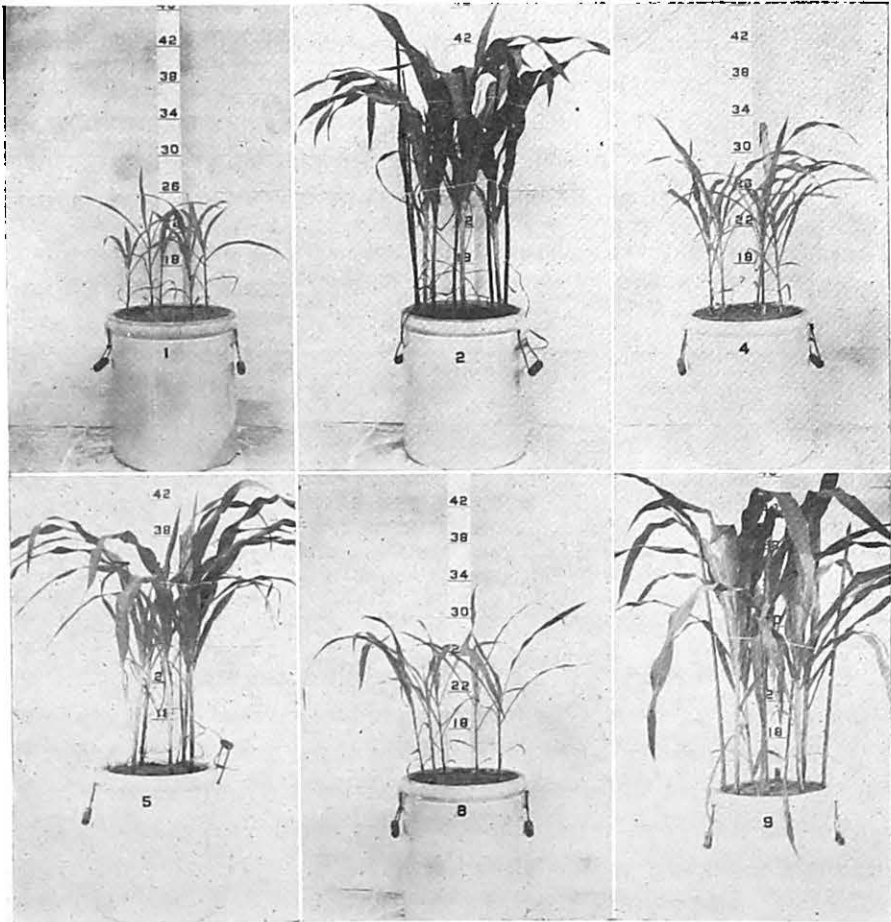


FIG. 1.—1, No manure. 2, Manure fermented. 4, Manure fermented and dried. 5, Manure, superphosphate before fermentation, dried. 8, Manure superphosphate after fermentation, dried. 9, Nitrogen, phosphate and potash (no manure).

superphosphate is spread on top of the manure just as it is hauled to the field.

Crop returns parallel nitrogen recoveries (plate 1). The highest yields were obtained when inorganic salts were used in amounts equal to the quantities of total plant nutrients in the undried manure. Their plant food was immediately available to crop uses, whereas much of the organic nitrogen in the manure, as well as other constituents, was not in readily available form.

DISCUSSION AND SUMMARY

Manure is a very perishable product. Material losses of plant nutrients, especially nitrogen, occur between the times when it is voided and when it is incorporated into the soil. The magnitude of some of these losses and the effect superphosphate exerts in reducing them are presented in this bulletin.

Storage losses have received much attention. These are often excessive in horse and poultry manures but are small, as compared with drying losses, in cow manure.

Manure is often hauled out in the spring just prior to seeding corn. If it is not promptly worked into the soil, nearly all of its available nitrogen may be volatilized as ammonia as a result of the drying effect of warm winds. Since even a little soil can hold much ammonia, prompt harrowing should follow spreading whenever possible for the manure then becomes coated with soil and subsequent drying losses are reduced. Much wastage also ensues when meadows and pastures are topdressed, especially during the summer, since manure dries out before the rains can wash the soluble and volatile nitrogen into the soil. Plant debris, such as stubble, aftermath, etc., often holds manure suspended above the soil level so that it does not come into close contact with the soil, in which position it readily dries out with much loss of nitrogen. If manure is to be thus used, it should be spread just before or during a rainy season rather than after rains have ceased.

Freshly voided cow manure contains very little ammonia. However, ammonium carbonate is quickly formed from urea and other easily ammonified compounds, more especially in the urine. Given proper temperature conditions and plenty of micro-organisms, most of the urea may become ammonified within a few hours. Since the stable gutters are apt to be quite warm and are always highly inoculated, and, since manure usually remains in the stable for at least 12 to 24 hours, much ammonification takes place and large amounts of nitrogen may be lost

by drying (or drying by freezing) even if daily haulage and spreading are practiced. Much loss may result in the winter due to freezing. When manure freezes, some of its water crystallizes as ice, the ammonia becoming increasingly concentrated. Freezing losses are smaller than those due to ordinary drying. Roughly half of the ammonia may be lost through freezing, whereas sometimes nearly all of it escapes when manure dries out.

This type of loss is not readily controlled; however, the use of superphosphate tends to lessen it; in fact, this is about the only amendment that may be used in actual practice. Different grades vary in their conservation abilities. Those containing much gypsum (16 and 20 percent superphosphates) are superior to that containing little (40 percent grade). While the granulated 20 percent grade contains more than any other phosphate used, it is not always the most effective. In its granulated condition it is less active and requires more time to complete the reaction, and if used should be thoroughly mixed with the manure. The granular goods, however, possess other virtues in that they are less dusty and less slippery when applied on stable walks.

Gypsum (calcium sulphate), when used alone, is of little service in conserving ammoniacal nitrogen, but works well when added to a phosphate. Its calcium is then partially removed in the precipitation of tri-calcium phosphate, leaving an equivalent amount of sulphuric acid to form a stable compound—ammonium sulphate. While phosphorus solubility is greatly reduced by the formation of tri-calcium phosphate, which is precipitated in a very finely divided form and in the presence of decaying organic matter, its availability is not materially reduced. On the other hand, it is quite possible that it may become even more available to plant uses in this condition since it is less easily fixed into non-available forms by the soil.

The effectiveness of superphosphate is enhanced by thorough admixture with the manure, which can be best accomplished in the gutter where the urine gets a better chance to dissolve and react with it. When applied to manure about to be hauled to the field, its efficiency is much impaired. It has less chance to dissolve and react, and much drying loss ensues. Furthermore, when it is added to ammonified or fermented manure, the carbonates which are present greatly interfere with its efficiency. When present in considerable quantities, much of the calcium precipitates as calcium carbonate instead of as tri-calcium phosphate, and ammonia is much less stable in the presence of the former than in that of the latter compound; an added reason why it is better to

apply superphosphate to manure before rather than after fermentation.

While superphosphate is quite efficient in conserving nitrogen, its theoretical value from a chemical standpoint greatly exceeds that obtained in actual practice. When 16 or 20 percent grades are treated with dilute ammonium hydroxide solution and then dried, they will hold about five percent nitrogen. Since well-ammonified or fermented manure contains about one-half of its total nitrogen (five pounds in a ton) in the form of ammonia, it is evident that 100 pounds of superphosphate per ton of manure should prevent all drying losses of nitrogen. This, however, was never accomplished, serious drying losses occurring notwithstanding applications of 100 pounds per ton and even with those of 300 pounds per ton, mainly because the manure is so viscous that the superphosphate does not get a chance to react completely with it. Then, too, it may be that micro-organisms take up proportionately more phosphorus than nitrogen into their structures. And, finally, some elemental nitrogen is always lost whether superphosphate is used or not.

While its use in the dairy barn is a chore, it should be remembered that practically every Vermont soil lacks available phosphorus. Usage in the stable is one way in which to supply this deficient element and would be worth while even if it had no other virtue. However, superphosphate has others. It lessens undesirable stable odors. When spread on the stable walks, it absorbs some moisture, helps to keep them dry, and reduces the number of flies. Bryan and Andrews (7) have found it a good disinfectant since it actually kills many micro-organisms when applied to the stable walks and floors.

It is apt to corrode bags, clothes, shoes, etc., if left in contact with them for a long time. For this reason, some have felt that it might injure the feet and hoofs of cattle. This is not likely to occur. There is always much ammonia present in the gutter or wherever there is liquid manure, which readily neutralizes the acid present in superphosphate.

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