NOTE.

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VALUE OF ORGANIC MANURES AND INORGANIC FERTILIZERS.

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INTRODUCTION.

Hunger is the oldest enemy of man. An adequate supply of food was the most important problem in the past as it is today. Famine and starvation were frequent amongst all nations due to failure of crops and it was accepted as an unavoidable evil. Only in recent years science and technology have been systematically applied for food production in Europe and America.

The acuteness of the problem in this country will be evident from the following considerations:

It is estimated that the total world production of cereals (wheat, corn, paddy, barley, *Jowar*, *Bajra*, *Ragi* and other grains) is approximately 600 million tons. Since 1911 the cereal production in India and Pakistan has remained practically constant at 60 million tons per annum. If the cereals produced in the world were equitably distributed amongst all the inhabitants of the earth, each one of us would have 3,300 calories per day. India and Pakistan consist of 1/5th of humanity but they produce only 1/10th of the cereals. The good food materials like potatoes, milk, butter, cream, cheese, meat, fish, eggs, etc., are produced in the whole world to the extent of 400 million tons. The production of these materials in India and Pakistan is much less than 1/10th of the world production. Hence it is no wonder that India is half fed.

It is clear, therefore, that food production in this country has to go up enormously both by intensive cultivation of the land under crops and by bringing new land under cultivation.

It is apparent that the use of manures and fertilizers has to be on a larger scale than at present. The aim of agriculture must be sustained production—production and conservation together; but we are now failing to achieve this aim. Some soils are declining in fertility and humus. Some are becoming hard. Erosion is taking a heavy toll. There is great need for making the utmost of our knowledge to increase production on a sustained basis. It is necessary, therefore, to understand which form of manure or fertilizer is most suitable.

The value of animal manure in improving the productiveness of land was recognized from the dawn of human history. The relative merits of the dung of birds and poultry and of the excreta of horses, cows, goats, sheep and men for different soils and crops were fully discussed by the agricultural writers of Græco-Roman times. The benefits of composts prepared from dung, urine, straw, stalks, leaves, weeds and other trash were emphasized. Green manuring was also recommended by the Roman author, Pliny (23–79 A.D.).

It is well known that the Greek Philosopher, Aristotle (384–322 B.C.) advocated that the four elements, fire, air, water and earth, formed the material constituents of the world. He also believed that plants derived nourishment through their roots from pre-formed organic matter in the soil.

Philippus Aureolus Theophrastus Bombustus Paracelsus von Hohenheim (1493–1541), the great German Iatro-chemist, modified the doctrine of Aristotle and declared that the material world consists of the three principles, sulphur, mercury and salt.

The first experimenter to tackle the scientific aspect of agriculture was Bernard Palissy (1510–1589), the celebrated French authority on ceramics, who had fairly clear ideas regarding the importance and storing of manures and the formation of salts like nitre from manures and the value of salts in crop production. According to Glauber (1604–1668) saltpetre or nitre is the greatest of all salts, being the salt of vegetables, animals and minerals.

Palissy, Bacon, Glauber and Boyle were supporters of the doctrine of Salt advocated by Paracelsus. On the other hand, there were several distinguished men, notably Home, Wallerius, Thaer, deSaussure, Davy, deCandolle, Berzelius, Mulder and others who were advocates of the Aristotelian doctrine of plant nutrition by soil organic matter.

Lavoisier (1743–1794), the founder of Chemistry and Physiology, was impressed by the value of growing grass in improving the fertility of land. He also studied the problem of the formation of saltpetre and the construction and operation of nitre beds on soils rich in nitre.

It will be interesting to state here that in 1665 Sir K. Digby reported that he had increased the yields of crops by the application of saltpetre. Little was understood regarding the principles of fertilization until 1804, when deSaussure first directed the attention of the scientific world to the fact that the ash ingredients of plants were taken from the soil and they were essential for plant growth. About 50 years later Liebig (1803–1873) the great German Chemist and founder of the mineral theory of soil fertility laid great emphasis upon the necessity of supplying plants with phosphoric acid and potash, but he missed the value of adding nitrogenous manures to the soil and he stated the position as follows in 'Farmers Magazine' in 1847:—

'If the soil be suitable, if it contains a sufficient amount of alkalies, phosphates and sulphates, nothing will be wanting. The plants will derive their ammonia from the atmosphere as they do carbonic acid.'

The great French chemist, Boussingault (1802–1887), founder of the quantitative agricultural chemistry, emphasized the importance of nitrogen in crop production in the following words:—

'Nitrogen is the element of the highest importance which it is necessary to increase and conserve in manure. The organic substances that are most advantageous for producing fertilizers are precisely those which give birth, by their decomposition, to the largest amount of nitrogenous bodies, whether soluble or volatile.'

Lawes, Gilbert and Pugh, working at the Rothamsted Experimental Station, established experimentally in 1857 that the addition of nitrogenous manures greatly improves crop production.

Bones were used for fertilization in England in the seventeenth century.

Peruvian Guano was used in England in 1820. Although the deposits of Peruvian Guano were discovered by Count Humboldt in 1802, its fertilizing value was recognized later on. The exploitation of Chile saltpetre was begun in 1830 with the help of British capital. Ammonium salts from coal distillation were prepared and utilized in 1840. The German potash salts were first introduced as fertilizers in 1860. Liebig demonstrated in 1840 that the fertilizing value of bone is increased by treatment with sulphuric acid. The Superphosphate Industry was founded by Sir John Lawes in 1843.

A large number of distinguished agricultural chemists attached great importance to the manurial value of salts in crop production. On the other hand, another group emphasized the importance of the organic matter or humus in agriculture and maintaining soil fertility. In the subsequent pages it will be shown that both minerals (salts) and organic matter are beneficial towards crop production.

FUNCTION AND VALUE OF ORGANIC MATTER.

It is now believed that plants can derive all their nutrients except carbon from the soil humus. Nutrients like nitrates, calcium, potassium, ammonium, phosphate, etc., can be supplied by the adsorbed matter remaining on the soil and humus surface; these nutrients are in equilibrium with the same ions existing in the aqueous phase of the soil. It is well known that the adsorptive capacity of soil humus is four times that of clay. It may be that the inorganic ions like nitrate, Ca, NH_4, PO_4, etc., present in the soil may be taken up by the wet humus derived from the organic matter and a part of these ions may pass into the aqueous phase to be readily adsorbed by crop roots. Moreover it has been stated that the inorganic fertilizers produce better results in soils containing more humus. It is certain that humus can supply almost all plant nutrients slowly but steadily to the growing crops. But for the supply of nitrate specially in cold countries, the humus must undergo oxidation either by better aeration or liming the material. Otherwise ammonia will be given out which may be washed away before nitrification. A soil rich in humus has not only more moisture but also it possesses porosity and a better chance of aeration which is of vital importance for plant roots. It is no wonder, therefore, that the chemists who tackled soil problems attached great importance to humus. In tropical countries the humus capital of the soil is very low and naturally the retention of inorganic salts in the soils when there is a heavy rain is likely to be endangered and hence the value of artificial manure cannot be pronounced in tropical countries with heavy rainfall. It has been observed in Malayan soils that ammonium sulphate does not improve crop production but farm-yard manure is much more profitable.

The response due to the application of ammonium sulphate in conjunction with other bulky manures like farm-yard manure, compost, etc., appears to be marked. Various experiments with green manuring have been conducted at different centres in India. Their results indicate that on poor land and lands of average fertility which is indicated by yields of 1,000 to 2,000 lbs. of paddy per acre, the response due to the application of 3,000 to 6,000 lbs. green leaves per acre is progressive. In experiments conducted at Berhampore (Orissa) a combination of green leaf with ammonium sulphate gave better yields than green leaf alone. So a green manure crop is not completely adequate in the supply of essential elements and it should be supplemented with artificial fertilizers like ammonium sulphate bone meals or superphosphates to get higher yields.

It has been proved beyond doubt that the major portion of paddy lands in India generally lack in organic matter which plays a great part in improving the fertility of soil and the primary requirement of paddy soil is nitrogen mostly in the form of humus. For tea soils Mann (1935) has stated, 'There is little evidence that liberal manuring with soluble nitrogenous manures can act as a substitute for organic matter as a source of nitrogen'. The green manures which have been successfully used in Ceylon, Java, Puerto Rico and Low Congo should be utilized in India where chemical fertilizers are yet unavailable. Crop yields can be maintained or increased by adopting better rotations by making full use of animal manures and crop residues and by using lime and green manure crops. Fertilizers are wasteful on farms not possessing a good cropping system.

One thing is clear from all European and American experiments regarding artificial fertilizers that when ammonium sulphate or nitrate or urea or sodium nitrate is added to crops with superphosphate and potash and usually with chalk yield of cereals, cotton and potatoes may be doubled using about 300–500 lbs. of mixed fertilizers per acre. But in a poor country like India this is far too costly unless Government supplies these materials at cheap price. When the humus capital of the soil is large, as in European soils, the artificial fertilizers are effective, but, in soils low in humus, artificial nitrogen seems to be much less effective as observed by workers in Bengal and Malaya. The reason of this essential difference seems to be that the humus, i.e., the mixture of protein and lignin or other organic matter possessing high adsorptive power can adsorb the ammonium ion, the nitrate ion, phosphate ion, potash and calcium ions, etc., and these adsorbed ions are liberated slowly for the benefit of the crops during the whole period of their growth. This adsorption and slow liberation of the nutrient ions avoids leaching of minerals including nitrates of soils when torrential rain falls. On the other hand, when inorganic salts are added to soils low in humus, the adsorption and retention is much less than in humus rich soils. Consequently, the washing away is rapid when rain falls. Under certain conditions with inorganic fertilizers, the growing plant may have an overdose of minerals and this may be harmful.

Bromfield, in his 'Pleasant Valley', has stated that near his farms many agriculturists added inorganic fertilizers every year without increasing the humus capital, and in most cases, as no lime was used, the soil became highly acidic and unfit for cultivation, but on green manuring with legumes, such land became fertile again. In Rothamsted experiments no increase in the humus content has been observed with artificial fertilizers although they increase crop production. The root system left in the soil is not enough to fix atmospheric nitrogen and enrich the soil appreciably. As the efficiency of nitrogen fixation by organic substances is almost as low as the efficiency in the industrial Haber-Bosch or Birkeland-Eyde process, i.e., only 1 to 10% of the energy obtained by carbon oxidation may be utilized in nitrogen fixation by adding organic matter, hence in order to increase the nitrogen status of the soil permanently, a large quantity of organic matter has to be added.

Another method suitable specially for Europe is the addition of inorganic fertilizers mixed with farm-yard manure, straw, leaves, sawdust or coal, etc., which can form humus and to bring the carbon-nitrogen ratio to about 11 or 12 so that the inorganic matter can be retained by the humus formed for longer period, i.e. semi-permanently in the soil. It seems that the adsorption of nutrient ions by the humus and clay and their slow liberation for the benefit of crops is one of the most important functions of humus because plants require nourishment during the whole period of their growth as will be evident from the following table:

TABLE I.

Percentage of Plant Food Adsorbed per acre by Potato Plants and Tubers during each period.

Period of growth (weeks).	Nitrogen.	Phosphorus P_2O_5	Potassium K_2O	MgO	CaO	Totals.
0– 7 ..	11	6	12	4	3	9
8 ..	6	7	6	6	7	6
9 ..	10	11	12	10	8	10
10 ..	24	22	24	20	17	23
11 ..	13	14	16	15	18	16
12 ..	32	34	24	29	17	28
13 ..	1	4	5	8	17	5
14 ..	3	2	1	8	13	3
Totals ..	100	100	100	100	100	100

'Organic matter in soil' is a very general term. It includes the living forms, roots, fungi, bacteria and small animals; fresh remains of living matter, a more or less stable decomposition product brown or black called 'humus' and a host of intermediate products. The final decomposition products are, of course, water, ash, carbon dioxide and a small amount of various gases. Perhaps the great importance of organic matter may best be realized by listing its functions in soils. The relative significane of the several items varies a great deal among different soil types. The supreme value of the additiôn of organic matter to soil is the fixation of atmospheric nitrogen and the preservation of the nitrogen present in or added to soil as has been established by Dhar and co-workers. The other functions have been well stated by C. E. Kellogg (1948) as follows:—

(1) 'Organic matter promotes granular structure and pore space in some soils. Thus it may aid root extension, promote entry of water into the soil, reduce soil washing, reduce soil blowing, promote aeration or exchange of gases, increase the water holding capacity and reduce baking and crust formation.

(2) It reduces evaporation especially when used in the surface or as a mulch.

(3) It reduces the extremes of temperatures, especially high summer temperatures when used as mulch.

(4) Humus aids in the maintenance of reaction (pH) in the soil by acting as a buffer.

(5) Organic matter aids in the retention of soluble substances including many plant nutrients, by holding them in living or nearly fresh forms against the forces of leaching and by the base exchange properties of humus.

(6) Part of organic matter furnishes a food supply for micro-organisms and small animals in the soil including forms essential for the transformation of nitrogen compounds and for other processes important in plant nutrition.

(7) Organic matter furnishes directly, and indirectly by promoting bacteria and fungi, complex organic compounds which may include both growth promoting and antibiotic substances. Very little indeed is actually known about the rôle of these compounds in soil productivity.

(8) Addition of organic matter especially from normal plants of mixed types maintain a slowly available, fairly well-balanced supply of plant nutrients including the micro-nutrients. This is very important everywhere but specially so in warm humid countries where leaching is severe and fertilizers expensive.'

Green Manures and Residual Effect.

The increased yields from turning under winter legume crops have ranged from 6 to 60% over the yields of check plots. In some southern states of U.S.A. cotton yields have been increased from 22 to 100% in various experiments and corn in south of America from 24 to 78%. Sweet clover is generally used in the south of U.S.A.; summer legumes are also beneficial. In middle-western states of U.S.A. residual effect has been observed for 8 to 10 years.

Carbon/Nitrogen ratio of some Organic Materials.

Material.	C/N Ratio.
Sweet clover (young)	12
Barnyard manure (farm-yard manure)	20
Clover residues	23
Green rye	36
Cane trash	50
Straw	80
Sawdust	400

Lignin makes up 40 to 45% of the total humus, and protein 30 to 35%, the remainder consists of fats, waxes and other residual matter. Phosphorus, sulphur, calcium, magnesium, potassium, iron and aluminium and other elements may be chemically bound or adsorbed with humus. Since lignin and protein account for 70 to 80% of the total humus, the formation of a lignin-protein complex suggests evidence to explain the more or less constant carbon-nitrogen ratio in mineral soil. If a ton of fresh organic matter (dry weight) in the form of green manure, farm manure or plant stubble is ploughed under or worked into the soil, decomposition begins immediately within a period of two or three weeks, under favourable conditions of moisture, temperature and aeration, only about ⅓ of the original ton may remain. Many soils are too low in fertility to produce good sod, cover crop or green manuring crop. With such soil conditions it is not possible to build up the humus content unless material from outside is brought in. The humus level in mineral soils is very closely associated with the supply of the nutrient elements such as calcium, potassium, phosphorus and nitrogen.

The solubility of CaO, P_2O_5, K_2O, MgO and other elements is increased through the effect of organic and inorganic acids produced from the decomposition of organic matter. The organic acids disappear by further oxidation.

The availability of nitrogen in ordinary farm manures is believed to be 25 to 30% of that of mineral nitrogen fertilizers but there is a residual effect; the availability of P_2O_5 and K_2O is essentially equal to that of mineral fertilizers. It has been demonstrated that the soluble humates in manure increase the solubility and mobility of mineral phosphates. Moreover, Thiamine Chloride (Vitamin B), Creatinine and other growth regulating substances are present in manure as also calcium, magnesium, sulphur, iron, manganese and other elements, which are valuable.

Data from Ohio Experimental station covering 30 years of cropping show that manure increased considerably the amounts of active calcium, magnesium, potassium, sodium and manganese in the soil compared to the quantities contained in unmanured soil. In most cases, however, even the application of 16 tons per 5 years rotation of manure did not maintain the supply of these elements at the original level. The lime requirement was not much affected by manure but all the plots were considerably more acid than at the beginning. The exchange capacity of the soil was increased.

Manure when used as a top dressing protects the soil from beating rains, decreases evaporation losses of water and appreciably improves the tilth of heavy soils. Incorporating manure with soil may be effective in reducing soil erosion by increasing the permeability of the soil to water, thus decreasing the run off losses and by increasing the density of the vegetative cover, which in turn decreases the rate of surface run off and increases water penetration. A large number of experiments has been reported showing that manure is effective in reducing both water and soil losses.

Nitrogen—the Key Element.

Recently Crowther and Yates (1941) have reported that the responses to phosphate and potash are substantially reduced when dung is applied but crops are equally responsive to inorganic nitrogen on dunged and undunged land. They reported large responses of crops on applying 10 tons dung per acre in absence of artificials. Thus the value of artificial nitrogen in enhanced by the addition of dung.

The question may well be raised as to why soil nitrogen content is made the basis for the fertility ratings of crops instead of phosphate or potash.

It must be remembered that nitrogen accumulates in soil in humid regions almost entirely in the forms of humus, which in turn is largely a product of the decay of plant tissues together with cells of micro-organisms. In other words, to accumulate humus it is necessary for soil conditions to be favourable for a considerable growth of plants including legumes. This growth in turn involves at least a moderate supply of all essential plant food elements, a favourable soil reaction and drainage condition and a reasonable amount of precipitation or irrigation water. On the whole, then, the nitrogen or humus content of a soil is a fairly accurate index of productivity.

REASONS WHY GRASS LAND IS RICHER IN NITROGEN THAN FOREST OR TIMBER LAND.

Dhar (1935) and co-workers have established that when molasses, leaves, straw, sawdust, peat, coal and other carbonaceous compounds with carbon-nitrogen ratio greater than 10 are added to the soil and allowed to undergo oxidation the energy obtained by the oxidation of the carbonaceous compounds is utilized in fixing the nitrogen of the atmosphere and synthesis of proteins and in this process sunlight is actually utilized in improving the nitrogen status of soils all over the world. It is well known that prairie soils or those covered with grass or other vegetation are richer in their humus and nitrogen contents than timber soils. This may be due to the fact that more sunlight falls on grass lands and helps in improvement of nitrogen status by fixation of atmospheric nitrogen from the oxidation of carbonaceous compounds than forest or timber soils. This is a very important new consideration which has to be emphasized. Moreover, the percentage of nitrogen is smaller in acidic soils than in neutral conditions and forest soils are likely to be more acidic than grass soils.

Dhar and co-workers have proved that when nitrogenous fertilizers or proteins are added to the soils under aerobic conditions, the following changes take place: Proteins$\rightarrow$Amino acids$+O_2\rightarrow NH_3+O_2\rightarrow NO_2+O_2\rightarrow NO_3$. It is known that these changes are oxidation processes which are accelerated and favoured by increased aeration and absorption of solar light. In these processes, the unstable substance, ammonium nitrite, is formed as an intermediate product and undergoes oxidation and decomposition aided by sunlight as follows:—

$$(a)\ 2NH_4NO_2+O_2\rightarrow 2NH_4NO_3$$

$$(b)\ NH_4NO_2\rightarrow N_2+2H_2O.$$

The second chemical change is more prominent than the first and hence there is considerable loss of nitrogen from soils when manured with the nitrogenous compounds. This is supported by results of field trials showing that the recovery of nitrogen by crops never exceeds 50%, whilst the recovery of phosphate and potash may easily go up to 85%. Lohnis and Fred have reported the following recovery in field experiments lasting for four years:—

Nitrogen	..	P_2O_5	..	K_2O
7·8 to 46·1%	..	10·1 to 75·6	..	22·4 to 85·1

Russell has stated that the recovery of ammonium sulphate when added at the rate of 1 cwt. per acre is as follows:—

Crops.	Average Nitrogen Recovery.
Wheat	39·0%
Barley	47·5%
Oats	46·5%
Potatoes	50·0%
Swedes	35·0%

Manure contributes to soil productivity through both its humus content and the plant nutrients supplied which stimulate crop growth. The two contributions may be considered equal in value in increasing the humus of the soil. The Missouri Experiment Station determined the effect of 6 tons of annual application of manures for 50 years on the nitrogen content of the soil that was growing various sequences of crops. The total increase in nitrogen content of the soil was 41·1%. As 300 tons of manure were applied, this makes an increase of 0·137% of nitrogen for each ton of manure. This is due to the fixation of atmospheric nitrogen in the oxidation of the manure.

In this connection, it is of interest to record the results obtained by White, Holben and Richen (1945) with 20 plot soils under continuous cultivation and under permanent grass. The unfertilized grass lands at the end of 72 years (1869–1940) show a nitrogen level 68·2% above the unfertilized plot soils and 42·1% above N P K treatment.

Russell (1931) has reported that the nitrogen content of a grass land increased from 0·152% in 1856 to 0·338% in 1912. Similarly a land permanently covered with vegetation for 24 years showed an increase in the nitrogen content from 0·108% to 0·145%. These results have been clearly explained by Dhar from the view-point that the cellulosic and other energy materials from the grass or other vegetation get mixed with soil and are slowly oxidized in the soil and in this process, nitrogen of the air is fixed and as copious sunshine falls on grass and prairie lands, the nitrogen fixation is much increased by absorption of solar light as has been observed by Dhar and co-workers.

Loss of Nitrogen from Nitrogen Rich Compounds.

From ancient times animal matter like blood, fish, bonemeal, tankage, wool-residues, meat-residues, guano, human excreta, etc., has been used as manure, but the mechanism of their action has been cleared up only in recent years. The carbon-nitrogen ratio of these substances is less than 10 and when they are mixed with soil, the carbonaceous compounds and the proteins are oxidized with the liberation of carbon dioxide and ammonia, which in its turn is further oxidized to nitrite and nitrate, which is the chief plant food material. The above-mentioned substances are known to be fairly quick acting manures in crop production. Researches carried on in the Allahabad University have established that when nitrogenous fertilizers are added to the soil, a good deal is wasted as nitrogen gas without benefit to the crop or soil. When 100 lbs. of ammonium sulphate are added per acre of land under cultivation, about 40 lbs. are available to the crop, but about 60 lbs. are wasted as nitrogen gas under ordinary conditions of cultivation. In our recent experiments the following results have been obtained with different nitrogenous substances:—

Table II.

Substances mixed with soil.	Period of exposure.	Loss of nitrogen %		Percentage loss of nitrogen in unit time (per month).	
		Light.	Dark.	Light.	Dark.
(1) Ammonium sulphate ..	2 months ..	55·5	43·2	27·8	21·6
(2) Ammonium phosphate	,, ..	67·5	58·2	33·8	29·2
(3) Ammonium nitrate ..	,, ..	28·9	21·0	14·5	10·5
(4) Ammonium tartrate ..	,, ..	47·6	38·3	23·8	19·2
(5) Ammonium oxalate ..	,, ..	36·6	28·6	18·3	14·3
(6) Ammonium citrate ..	4½ ,, ..	69·9	54·8	22·1	12·2
(7) Urea	5½ ,, ..	47·4	35·1	10·5	7·8
(8) Hippuric acid ..	4½ ,, ..	42·3	23·2	9·4	5·2
(9) Gelatine	4½ ,, ..	40·1	23·2	8·9	5·2
(10) Oil-cake	5½ ,, ..	35·9	29·0	6·5	5·3
(11) Blood	6 ,, ..	54·1	48·7	9·0	8·1

The amount of nitrogen initially present in the above nitrogenous compounds varied from about 0·25 gram to 0·5 gram in 100 grams of soil. Moreover, with such manures acidity is produced. With ammonium nitrate better results is expected and obtained because half of the nitrogen is in the form of nitrate and hence the loss is less than with ammonium sulphate. With ammonium nitrate no acidic residue is added to the soil permanently as the nitrate ion is either absorbed by the plant or leached away in the underground soil. With sodium or potassium nitrate certainly better results are expected but when the carbonaceous substance in the soil is large there is always the possibility of the formation of nitrite and perhaps ammonium salt and thus loss of nitrogen as nitrous acid and nitrogen gas specially in acid soils and there is considerable leaching with nitrates. Hence these inorganic fertilizers although they are quick-acting and readily available in our industrial civilization do not enrich the soil permanently as there is hardly any addition of humus with such fertilizers. The great advantage with such fertilizers is that they can be added to the growing crop or as a top-dressing material and no time interval is needed between the addition of the fertilizer and the sowing of the crop. The disadvantages are (1) much loss of nitrogen in the gaseous state specially with ammonium compounds, (2) the production of acidity, (3) leaching, (4) no humus addition, (5) and specially in our soil which is on the alkaline side, there is the possibility of a loss as ammonia gas.

Fixation of Atmospheric Nitrogen in Soil and Formation of Humus.

For over 20 years we have been utilizing different energy producing materials in enriching the soil from the nitrogen point of view. We have tried all the sugars and observed that when they are mixed with soil, they are oxidized finally into carbon dioxide and water with the liberation of energy which is utilized in fixing the nitrogen of the air on the soil surface. If the system is illuminated by sunlight or artificial light, the light is absorbed by the system and the nitrogen fixation is greatly increased. This utilization of light in enriching the soil takes place under natural conditions all over the world and appears to be next in importance to photosynthesis in plants. We have utilized all sugars, starch, glycerol, filter paper, lignin, butter, melted and clarified butter known as *Ghee* in India, and found that all these materials though may be free from nitrogen undergo slow oxidation in soil in presence and absence of sunlight. In all these cases nitrogen increase to the soil takes place without the addition of nitrogenous manures. We have also observed that molasses, press mud, plant residues, leaves, farm-yard manure, cow dung, straw, cotton-wool, saw-dust, etc., with carbon-nitrogen ratio varying from 400 to 20 not only add the nitrogen they contain but fix atmospheric nitrogen as well. The fixation of nitrogen is greater, the greater the carbon-nitrogen ratio of the energy material. In this process also sunlight or artificial light is utilized in improving the nitrogen status. Marked fixation also takes place under sterile conditions. The carbonic acid and other acids produced in this process help in making the minerals present in plant materials and in soils soluble and readily available to crops.

On the application of farm-yard manure in Rothamsted for a number of years the soil nitrogen which was originally 0·122% rose to 0·236% from 1842 to 1914. Repeated additions of ammonium sulphate or sodium nitrate did not improve the nitrogen status of soils at all. Similar results as recorded in Table III were obtained by us at Allahabad. Moreover, there is more nitrogen in the soil covered with grass than when there is no grass cover.

It is interesting to note that the percentage of nitrogen in the fields rose from 0·0386% to 0·094% after the first application of cow dung and to 0·1517% on the

TABLE III.

Soils.	Total C%	Total N%	NH_3 N%	NO_3 N%
(1) Not covered with grass	0·386	0·0388	0·0024	0·0012
(2) Covered with grass	0·633	0·0630	0·0039	0·0021
for months 6	0·658	0·0656	0·0039	0·0029
(3) Covered with grass for the whole year ..	0·790	0·0786	0·0051	0·0025

second addition and to 0·2000% after the third application of cow dung. The corresponding results with Neem (Melia Azadiractta Lina) leaf are as follows:—

Original nitrogen content .. .. .. 0·0386%
After first application .. .. 0·0628%
After second application .. .. .. 0·0815%
After third application.. .. .. .. 0·1021%

In every case the carbon-nitrogen ratio of the soil was allowed to attain the value 10 before the next application of the carbonaceous compound.

The foregoing results show conclusively that repeated applications of cow dung and neem leaf spread out in three years .enrich the soil markedly by incresing its nitrogen content and humus by fixation of nitrogen and retaining the added nitrogen as well, i.e., the nitrogen of the materials added. This process is aided by absorption of solar light. By the use of municipal rubbish, the nitrogen content of the soil was raised from 0·04% to 0·25%. Exeellent crops have been obtained in such improved lands.

It is estimated that 35 billion kilograms, i.e., 34,750 million tons of cellulose containing 13,750 million tons of carbon are added every year to the earth. From our experiments we find that 40% of the carbon is oxidized in our climatic conditions in four or five months and even if the same amount be taken to be oxidized on the surface of the earth in the whole year, it would mean that 5,500 million tons of carbon are oxidized every year. On a moderate estimate of 15 mgms. nitrogen fixation per gm. of carbon oxidized in sunlight about 82·5 million metric tons of nitrogen are added to the earth by fixation when 40% of the carbon

TABLE IV.

Condition.	Material used.	Period of exposure (Months).	Carbon oxidized % during the whole period.	Carbon oxidized % during one month.	Amount nitrogen fixed in mgm. per 100 gms. of soil.	Efficiency in sunlight, i.e. the amount of nitrogen fixed in milligrams per gram of carbon oxidized.
Unsterile ..	Cow dung ..	4	0·475	0·119	9·8	20·7
Sterile ..	Cow dung ..	4	0·303	0·076	4·6	15·2
Unsterile ..	Neem leaf ..	4	0·402	0·101	9·1	22·6
Sterile ..	Neem leaf ..	4	0·221	0·055	2·8	17·2
Unsterile ..	Wheat straw ..	12	0·605	0·050	14·2	23·8
Sterile ..	Wheat straw ..	12	0·319	0·026	5·5	17·4

The efficiency in the dark is half of that in sunlight.

added is oxidized. We can conclude that out of total 82·5 million tons at least 50%, i.e., 41·25 million tons of nitrogen are fixed in soils by absorption of solar light. The total output of nitrogen fixed synthetically in the factories of the world in 1937 was 3·54 million tons, i.e., 1/12th of what is obtained by fixation under natural conditions by the utilization of sunlight only with cellulosic matter.

It is interesting to note that although the velocity of oxidation of organic matter in sterile condition is smaller than in unsterile conditions, the efficiency of nitrogen fixation, that is, the amount of nitrogen fixed in milligrams per gram of carbon oxidized in sterile conditions, is of the same order as that in the unsterile experiments as is clear from the experimental results (Table IV).

Elements Present in Plants and Coals.

According to G. Bertrand (1938) a flowering lucerne plant contains the following elements:

Carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorus, chlorine, silicon, calcium, magnesium, potassium, and sodium varying from 45·37 to 0·157% whilst the following elements are present in smaller amounts ranging from 0·0036 to 0·0000027%: iron, aluminium, boron, copper, zinc, manganese, fluorine, titanium, bromine, nickel, molybdenum, iodine and cobalt. Moreover, V. M. Goldschmidt (1935) and others have reported the presence of the following elements in coal:

Carbon, hydrogen, oxygen, nitrogen, sulphur, potassium, phosphorus, chlorine, silicon, calcium, iron, manganese, sodium, titanium, zirconium, zinc, lead, cadmium, copper, gold, silver, vanadium, beryllium, germanium, nickel, barium, gallium, strontium, boron, scandium, yttrium, lanthanum, cobalt, molybdenum, uranium, arsenic, antimony, tin, iodine, bismuth, rhodium, palladium and platinum.

Elements Present in Soil.

A fertile soil contains the following:

Carbon, hydrogen, nitrogen, oxygen, phosphorus, potassium, calcium, magnesium, sodium, boron, copper, iron, manganese, zinc, cobalt, aluminium, titanium, molybdenum, chlorine, fluorine, iodine, sulphur and silicon.

It is clear that for the healthy growth of a crop the soil must contain those elements which form essential ingredients of plant life.

From ancient times plant materials have been partially decomposed in heaps or in pits and converted into composts which are added to the fields as manure. The aim of composting is *to conserve the nitrogen present in the plant materials* and add it to the soil with about 10 times its weight of carbon in the form of humus which also contains most of the mineral matters present in the plant residues along with micro-organisms.

Since 1936, Dhar has emphasized that the direct addition of plant materials to the fields before composting is more beneficial to crops, because the energy materials like carbohydrates, celluloses, lignin, fats, etc., when added to the soil, are partially oxidized and in this process nitrogen of the air is fixed and protein synthesis takes place. The value of the plant residues when added directly is due not only to their nitrogen content but also to the nitrogen fixed from the partial oxidation of their carbonaceous constituents. Hence much more humus (which is a combination of protein with lignin or cellulose or carbohydrate mixed with micro-organism) is formed and added to the soil when plant materials are mixed with the soil direct instead of their addition after composting elsewhere. The method of direct addition of plant materials to soils without composting has been adopted in farms in Pennsylvania and California, U.S.A. and England. The Citrus fruit industry in Palestine is utilizing the direct addition of fruit and plant residues to the soil under the advice of Dhar in enriching the field.

The chief artificial fertilizers used in industrially advanced countries are potassium salts, phosphates and ammonium salts, urea and nitrates, and for acid soils, calcium carbonate. It is clear that the above fertilizers do not supply all the materials required for the healthy growth of a plant. On the other hand, plant residues when added directly, or as compost, supply all the materials needed for plant growth. Dhar and co-workers have shown that carbohydrates, celluloses, lignins and fats act as marked negative catalysts in the oxidation of proteins and ammonium salts or urea to nitrites and nitrates. Hence the proteins added along with plant materials liberate nitrate much more slowly for the benefit of the crop and for a longer period than ammonium salts or urea. The slow liberation of nitrates from humus decreases the chance of leaching away of nitrates from soil. Proteins also undergo oxidation and partially lose their nitrogen but in the presence of carbohydrates, celluloses, lignin and fats, the loss is slowed down and hence the crop can absorb the nitrate formed slowly for a longer period.

Nitrogen fixed with Coal.

We have observed that peat, lignite and bituminous coal when mixed with soil in a very finely divided condition are slowly oxidized and in this process fixation of nitrogen takes place. The estimated total nitrogen capital of the world peat and lignite is 47,350 million tons. Moreover, the carbonaceous compounds present in coal are more inert than those existing in fresh plant materials, and hence, when finely divided coal is added to the soil, the available soil nitrogen is not readily converted into microbial proteins as with freshly added plant residues. Hence finely divided coal can be mixed with soil and crops can be grown almost immediately without giving any time interval which is needed when plant materials are added directly to the soil.

The growing of paddy and wheat has been found to be benefitted in our experiments by the addition of finely divided lignite and bituminous coal, which add nitrogenous manures and minerals needed for the growth of crops.

It is estimated that the nitrogen content of the humus in the top one foot of the cultivated lands of the world is 40,000 million tons. The amount of nitrogen fixed in all the nitrogen industries of the world was 3·54 million tons in 1937. Hence, the nitrogen still present in the world soils in the first foot from the top is 11,250 times greater than the yearly nitrogen production.

It is no wonder, therefore, that only 3 per cent of the world crop yield has been attributed to artificial nitrogenous manures in the last British Association meeting and reported in *Nature*, 1949, Vol. 164, No. 4171, page 597, as follows:—

> 'At present only some 3% of the world food production can be attributed to the use of nitrogenous fertilizers. To raise the food by 10%, that is to say one hundred million tons, involves a fourfold increase in supplies of fixed nitrogen at an approximate capital cost of £1,50,00,00,000 (2,100 crores of rupees). This would take a minimum of 15 years to achieve.'

Thus humus nitrogen is the chief nitrogen source of the world food production.

It is interesting to note that even in the highly industrialized countries, the amount of artificial nitrogen added per acre of land before the Second World War, was much less than the nitrogen requirement of even one crop per year as shown below in pounds of nitrogen added per acre of land under cultivation:—

> Belgium (28·5), Holland (24·8), Germany (15·6), Denmark (10·3), Norway (6·0), Sweden (5·24), Italy (4·3), France (4·0), Great Britain (2·5), U.S.A. (1·36), Poland (0·73) and Hungary (0·15).

Moreover, in recent experiments, Dhar and Ghildyal have shown that in composting straw with 1/8th of its weight of soil, 37% of the initial nitrogen was fixed, whilst with pine needles under similar conditions 19·2% nitrogen fixation was observed. Nitrogen fixation was also observed both in sterile and unsterile condition in composting cow dung with small quantities of soil. It appears, therefore, that when the nitrogen content of a system is not large, the slow oxidation of carbonaceous compounds in presence of small amounts of soil, leads to fixation of atmospheric nitrogen more in light than in dark.

Sewage from the city of Melbourne, Australia, is used to good effect in the Metropolitan farm, Werribee. There is plenty of scope for manuring our land with sewage water of our cities. The following beneficial results were obtained in the soil of the Metropolitan farm :—

TABLE V.

Percentage composition of dry soil.

	Before irrigation. 1912	After irrigation.	
		1924	1938
Nitrogen N	0·13	0·26	0·50
P_2O_5	0·05	0·17	0·25
K_2O	0·15	0·80	1·09
CaO	0·06	0·32	0·39

ORIGIN OF NITRATE BED FORMATION IN NATURE.

It has been already reported that when nitrogen rich organic substances like blood, meat meal, urea, allantoin, uric acid, hippuric acid, gelatine, guano, oil-cakes, etc., are added to the soil, the nitrogenous materials are converted into ammonia and nitrates and a good deal of nitrogen undergoes loss as nitrogen gas. Hence, in the nitrification of carbonaceous compounds with carbon-nitrogen ratio smaller than 10, at least two types of substances are found: (i) nitrates like those of ammonium, calcium, sodium, potassium, magnesium, etc., depending on the concentration and availability of the minerals present in the soil, and (ii) humus, the composition of which depends on the nature of the organic substance mixed with the soil. Urea, however, does not add humus to the soil but only forms nitrates. Dhar and co-workers have shown that humus formation takes place not only by the combination of lignins and proteins but humus is also formed by the combination of microbial protein or soil or plant or animal protein with carbonaceous substances like carbohydrates, celluloses, fats, resins, waxes, etc., mixed with colloidal carbon. Hence, when blood, meat meal, fish, allantoin, uric acid, guano or other bird or animal excreta are allowed to undergo slow oxidation in air and light in presence of sand or soil or silicates, a large amount of nitrogen is lost in the gaseous state, along with the formation of sodium, potassium, ammonium, calcium, magnesium nitrates. It is clear, therefore, that the formation of nitrate beds, as in Chile, Bengal, Russia, Canada, U.S.A., and other parts of the world, is usually caused by the photo-chemical and bacterial nitrification of organic materials with a carbon-nitrogen ratio less than 10. It seems unlikely that the sea-weeds or plant materials alone, with a carbon-nitrogen ratio greater than 10, can readily form the nitrate beds as has been postulated. Sea-weed, mixed with fish or animal body or animal or bird excreta, can be the true source of nitrate beds.

On the other hand, carbonaceous substances like plant residues, straw, farmyard manure, etc., having carbon-nitrogen ratios much greater than 10, cannot be converted into nitrates readily like compounds having carbon-nitrogen ratio less than 10. When carbonaceous substances with carbon-nitrogen ratio much greater than 10 are allowed to undergo oxidation in soil or in sand, the carbohydrates, celluloses, fats, waxes, resins, lignin, gums, etc., are first oxidized slowly and in this process nitrogen fixation and small amounts of protein synthesis takes place. This process goes on till the carbon-nitrogen ratio of these materials becomes narrower and attain the value 10, that is, the carbonaceous materials are converted into humus. Humus when mixed with soil slowly undergoes oxidation into carbonic acid and ammonium salts which undergo further oxidation to nitrates. It is clear, therefore, that humus, formed from carbonaceous substances having carbon-nitrogen ratio greater than 10, can serve as a supplier of small quantities of nitrate. On the other hand, nitrogen rich materials like blood, meat meal, fish meal, urea, etc., when added to soil or sand can supply larger concentrations of nitrates to plants and are known as quick-acting manures and they behave as mixtures of nitrates and humus having a carbon-nitrogen ratio of the order of 10.

Humus as a Source of Nitrate.

It has been definitely shown in these laboratories that the available nitrogen in tropical soils is usually more than 10% of the total nitrogen. In other words, in the alluvial soils of the Gangetic plain the available nitrogen, i.e., ammonium salts and nitrates, can be 100 lbs. of nitrogen per acre with about 1,000 lbs. of total nitrogen. In soils of temperate climates, the ammoniacal and nitric nitrogen hardly exceeds more than 2% of the total nitrogen which is usually 0·15% making about 2,500 lbs. of total nitrogen per acre. When farm-yard manure has been added year after year the total nitrogen has gone up to 0·25% in the classical Rothamsted experiments. Such dunged soils become steady suppliers of 100 lbs. or more of available nitrogen per acre for the benefit of the crop.

The addition of ammonium sulphate to soils causes the production of nitrates with loss of nitrogen in the gaseous state, but no formation of humus takes place. The introduction in soil of nitrogen rich organic substances forms nitrate and small quantity of humus, and there is also loss of nitrogen in the gaseous state. But the addition of carbonaceous substances containing small amount of protein causes only the formation of humus which in large concentration can behave as an adequate source of nitrate necessary for the proper crop growth. It is clear, therefore, that humus adds steadiness to the soil and can behave as a suitable supplier of plant food materials. From the banking point of view, the humus capital of soil formed by the addition of carbonaceous materials with carbon-nitrogen ratio greater than 10 can be compared to the fixed deposit amounts in banks, whilst inorganic fertilizer producing nitrates liable to be readily leached away resembles money in current accounts. It is evident that animal urine can be readily nitrified and forms nitrates and thus can behave as supplier of salts, but only the dung producing humus cannot be supposed to contain much salt as was done by Bernard Palissy, Glauber and ancient agricultural chemists.

Summary.

(1) Figures showing the acuteness of the food situation in this country have been recorded.

(2) From an historical survey of the writings of the renowned chemists of the 16th, 17th, 18th, and 19th centuries, it is clear that a large number attached great importance to the manurial value of salts in crop production. On the other hand, another group emphasized the importance of organic matter or humus in agriculture and maintaining soil fertility.

(3) Both organic matter and soil humus and salts are beneficial to crop production.

(4) The parts played by humus in maintaining soil fertility and improvement of crop production, water retention capacity and avoiding water run off and erosion have been clearly stated:

Lignin makes up 40 to 45% of the total humus and protein 30 to 35%; the remainder consists of fats, waxes, and other residual matter, phosphorus, sulphur, calcium, magnesium, potassium, iron and aluminium and others may be chemically combined or adsorbed with

humus. Since lignin and protein account for 70 to 80% of the total humus, the formation of a lignin-protein complex suggests evidence to explain the more or less constant carbon-nitrogen ratio in mineral soil.

(5) Humus liberates nitrates more slowly than ammonium salts and other quick-acting manures and benefits the crop for a longer period. It seems that the adsorption of the nutrient ions by humus and their slow liberation for improving crop production is one of the most important functions of humus, because plants require nourishment during the whole period of their growth.

(6) The reasons why nitrogen is considered as the key element in plant production have been stated.

(7) An explanation has been given as to why the nitrogen content of forest and timber soils is less than in grass soils.

(8) The various processes by which nitrogenous fertilizers undergo nitrification are accelerated by aeration and absorption of solar or artificial light and there is marked nitrogen loss in nitrification. This conclusion is supported by results of field trials showing that the recovery of nitrogen by crops never exceeds 50% while the recovery of phosphate and potash may easily go up to 85%.

(9) Experimental results have been recorded showing marked loss of nitrogen in the gaseous state by the addition of ammonium salts and other quick-acting introgenous fertilizers to soils.

(10) When plant materials, farm-yard manure, straw, saw-dust etc., with carbon-nitrogen ratio greater than 10, are added to the soil, the fixation of atmospheric nitrogen and protein and humus formation take place. The addition of humus to soil by this process is much greater than when such substances are added to soil after composting them elsewhere. It has been observed that sunlight or artificial light is utilized in nitrogen fixation and humus formation and that the greater the carbon-nitrogen ratio of the starting material the greater is the nitrogen fixation and formation of protein and humus. This fixation is the chief source of soil nitrogen and the main function of the addition of organic matters to soils. In composting straw, pine needles, cow dung, etc., with small amounts of soil appreciable nitrogen fixation is observed, more in light than in dark.

(11) Much more nitrogen is fixed in the arable soils of the world by the absorption of solar light per year than the nitrogen fixed in all industrial operations. This nitrogen fixation can take place under completely sterile condition both in light and dark, more in light than in dark.

(12) The greater the fixation of nitrogen and humus formation in the soil, the greater is the residual effect of the manure.

(13) The efficiency of nitrogen fixation by the addition of organic substances is as low as the efficiency in the industrial Birkeland-Eyde or the Haber-Bosch process. Not more than 1–10% of the energy obtained by the oxidation of the carbonaceous substances is utilized in nitrogen fixation and protein synthesis by adding organic matter. Hence in order to increase the nitrogen status of the soil permanently, specially in tropical countries where oxidation processes are vigorous, a large quantity of organic matter has to be added.

(14) On the application of farm-yard manure in Rothamsted for a number of years the soil nitrogen which was originally 0·122% rose to 0·236% from 1843 to 1914. Repeated additions of ammonium sulphate or sodium nitrate did not improve the nitrogen status of soils at all. Similar results were recorded at the Missouri Experimental Station. We have been able to obtain exactly similar results at Allahabad when the total nitrogen in fields rose from 0·0386% to 0·094% after the first application of cow dung and 0·1517% on the second addition and to 0·200% after the third application of cow dung spread out over three years. By adding municipal rubbish with a carbon-nitrogen ratio much greater than 10, the nitrogen content of a soil increased from 0·04% to 0·25% and produced a bumper crop.

We have also shown that there is more nitrogen in soils covered with grass than in land without a grass cover.

(15) Another method for improving the nitrogen status is the addition of inorganic nitrogen fertilizers or urea mixed with carbonaceous substances like farm-yard manures, straw, leaves, saw-dust, peat, lignite or bituminous coal which can form humus and to bring the carbon-nitrogen ratio of the mixtures to 11 or 12 so that the ammonium and nitrate ions can be retained by the humus formed for a longer period in the soil.

(16) Considerable quantities of humus are present in peat, lignite and coal. These materials improve crop production by their slow liberation of nitrate and fixation of atmospheric nitrogen. These are also beneficial to alkaline soils.

(17) The method of direct addition of plant materials without composting is easier and more profitable as there is nitrogen fixation and more humus formation than composting, and has been adopted in farms in Pennsylvania and California, U.S.A. and Great Britain and by the citrus fruit industry in Palestine.

(18) Only three per cent of the world food production has been attributed to artificial nitrogenous fertilizers. Thus humus nitrogen is the chief nitrogen source of the world food production.

(19) The pounds of artificial nitrogen added per acre of land under cultivation varies from 0·15 in Hungary to 28·5 in Belgium and is much less than that required for the production of one crop per year.

(20) When blood, meat meal, fish, hippuric acid, uric acid, guano or other bird or animal excreta are allowed to undergo slow oxidation in air and light in presence of sand or soil or silicates, a large amount of nitrogen is lost in the gaseous state along with the formation of sodium, potassium, ammonium, calcium, magnesium nitrates, etc. It is clear, therefore, that the formation of nitrate beds as in Chile and other parts of the world is caused by the photochemical and bacterial nitrification of organic materials with a carbon-nitrogen ratio less than 10. It seems unlikely that the seaweeds or plant materials alone with a carbon-nitrogen ratio greater than 10 can form the nitre beds as has been postulated. Seaweeds mixed with fish or animal body or animal or bird excreta can be the true source of nitrate beds.

On the other hand, carbonaceous substances like plant residues, straw, farm-yard manure, etc., having carbon-nitrogen ratios much greater than 10 cannot be converted into nitrates readily like compounds having a carbon-nitrogen ratio much less than 10. When carbonaceous substances with carbon-nitrogen ratio much greater than 10 are allowed to undergo oxidation in soil in sand, the carbohydrates, celluloses, fats, waxes, resins, lignin, gums, etc., are first oxidized slowly, and in this process nitrogen fixation and small amounts of protein synthesis take place, and the synthesized protein and the protein added with the plant materials are protected by the carbohydrates, fats, etc., from rapid nitrification and partial loss.

References.

Bertrand, G. (1938). *Ier Congress International des Engrais Chimiqnes, Rome*, 3–6 (October).
Crowther, E. M. and Yates, F. (1941). *Emp. J. Exp. Agric.*, **9**, 77.
Dhar, N. R. (1935 and 1937). Pres. Address, Nat. Acad. of Sciences, India (Dec. 19 and Jan. 15).
Goldschmidt, V. M. (1935). *Ind. Eng. Chem.*, **27**, 1100.
Kellog, C. E. (1948). *Scientific Monthly*, **66**, No. 6, June.
Mann, H. H. (1935). *Imp. Bur.* of *Soil Science, Tech. Communication*, No. 32; Tea Soils, p. 28.
Russell, E. J. (1931). Soil Conditions and Plant Growth, 362.
White, J. W., Holben, F. J. *and* Richer, A. C. (1945). *J. Amer. Soc. Agron.*, **37**, 21.

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