Some Aspects of the Chemistry of Swamp Soil.

By Prof. V. Subrahmanyan, D.Sc., F.I.C.,
Indian Institute of Science, Bangalore.

THE study of swamp soil is of considerable practical importance and has a direct bearing on both agriculture and public health. The related problems are so numerous and so varied in character that they offer scope for all branches of science. Their solution will unravel the mystery which still surrounds the nutrition of the rice plant and will throw fresh light on the nature of life and life processes in the submerged soil.

It will be beyond the scope of a brief review to deal with all the related problems, so the present article is confined to certain chemical aspects having a bearing on the nutrition of the rice plant.

The agricultural operations connected with the cultivation of rice are generally well known and do not require any repetition. It may be pointed out, however, that some of them would require revision, or at any rate, better control in the light of recent scientific findings.

It is generally well known that in certain regions—especially in river deltas—the yield of rice is maintained at a fairly high level though practically no manure is applied. Even in the same locality, certain fields are known to be consistently more fertile than others though they may lie very close to each other. This difference is largely traceable to the extent of deposition of silt, some areas receiving more than others.

The biochemistry of river silt has not yet been adequately studied. The quantity of silt carried by each river, the amount deposited in different seasons, its distribution over the irrigated field, and its contribution to the succeeding crop—all these are important problems which are still awaiting solution. There is no doubt that some of the silts are quite rich and contain over 3,000 parts per million of nitrogen. There is also evidence to show that river silt facilitates oxidation changes.[1] Further studies in this direction may yield highly fruitful results.

In recent years, evidence has been adduced to show that one of the probable causes for the preservation of the fertility of the swamp soil is through fixation of atmospheric nitrogen. The fixation may be in symbiosis with the plant[2] or through the agency of free living organisms.[3] These researches are worthy of extension, with adequate crop experiments to check the various findings. The influence of various external factors—especially deposition of silt—on the nitrogen content of soil should also be determined.

There is evidence to show that, under submerged conditions, the mechanical composition of the soil is altered. The finer fractions tend to increase at the expense of the coarser ones. This has been traced[4] to the decomposition of organic matter (through biological agencies) resulting in the dissolution of minerals (chiefly iron and aluminium) present in the coarser fractions and their subsequent re-precipitation in the finer form. It would be of interest to follow the bearing of this on the increased heaviness observed in some of the areas which have been continuously under rice cultivation.

Some earlier workers[5] have reported that even mere increase in the moisture content of the soil leads to loss of nitrates and even total nitrogen. This is not supported, however, by later researches,[6] which show that when an uncultivated soil or one which has been fallowed for some time is water-logged, there is very little change in total nitrogen. The nitrate content (which is generally small) is further lowered and there is slight increase in nitrites. The most significant change is the production of ammonia, a large part of which is ordinarily retained in the soil sediment: very little passes into the supernatant, so that loss by leaching is comparatively small. If the water level goes down and the soil is exposed to dry, then a considerable part of the ammonia in the soil system is lost by volatilisation.

The mechanism of production of ammonia in the submerged soil has not yet been fully[7] understood. Evidence has been adduced to show that it is derived through degradation of plant residues and disintegration of microbial cells. Although the living organisms do not increase, the enzymes associated with them (especially the deaminase) bring about the desired change. In a manured soil, however, the changes are more complicated, as will be seen in a later section.

In the absence of freshly decomposing organic matter, the biological oxygen demand of the submerged soil is comparatively small. There is slow but steady movement of dissolved oxygen from the surface water into the soil below.[8] The conditions are considerably altered in presence of unrotted organic matter. The dissolved oxygen is very rapidly used up and the medium gets saturated with carbon dioxide and other gases.[9] The conditions become definitely anaerobic, and it is not until the completion of the fermentation that the oxygen of the atmosphere enters the soil system. On prolonged exposure, the dissolved gases pass out into space and aerobic conditions are then restored. In field practice, this process takes 3–5 weeks (depending on the nature of the soil and the amount of organic matter applied) for completion. The land is then fit for the crop.

The production of gases during decomposition of organic matter in the swamp soil has been the subject of a number of enquiries. The most outstanding contributions in the line are those of Harrison and Aiyer.[10] Working with the green-manured soils of South India, those authors showed that the chief gases produced during the fermentation are methane, hydrogen, carbon dioxide and nitrogen. These, on rising to the surface, encounter some active, aerobic bacteria, which oxidise methane to carbon dioxide and hydrogen to water. Carbon dioxide is taken up by the green algæ present at the surface of the soil and oxygen is released.

In this manner, the undesirable gases are removed and only oxygen and nitrogen are evolved from the soil system. Evidence has also been adduced to show that plant roots assist in facilitating oxidation changes in the soil.

Shortly after ploughing in the organic manure (generally a green manure), gas production begins. There is steady evolution over a number of days. The soil is then unfit for the crop : in fact, any that may be planted will be readily killed out. After the initial fermentation has largely subsided, then the algæ become prominent. The oxidation changes reported by Harrison and Aiyer are also noticeable during this period.

The manner in which the rice plant obtains its air supply has interested a number of workers, but no conclusive evidence has so far been obtained. Only the dissolved oxygen of the surface water is available to the root system and it is generally believed that the roots are highly adaptable and can function in the same manner as those of aquatic plants. In this connection, it may be mentioned that the plant thrives well only if a gentle flow of water is maintained. Prolonged stagnation of the surface water affects the growth and depresses the yield. Too great a depth of water is not beneficial to the crop, though certain varieties are able to stand it better than others.

Together with the gases, varying quantities of organic acids are produced in the soil system. The acids are chiefly lactic, acetic, propionic and butyric.[11] The first acid to be formed, and the one which is often produced in the largest amounts, is lactic acid. After a week or ten days, the quantity of lactic acid diminishes and is followed by increase in the other three acids. It may be said, in general, that if air supply is favourable, there is increased production of acetic acid : if unfavourable, greater quantity of butyric acid is produced. The chemical and biological mechanism of the production of acids, as also their bearing on plant growth, are still obscure.

Several workers[12] have drawn attention to the adverse effect of applying nitrates, especially during the puddling period, to the swamp soil. This is largely due to the formation of nitrites in the presence of fermentable organic matter. It is stated that nitrites are highly toxic if present in more than minute quantities. In addition to this, a considerable part of the soluble nitrogen will be immobilised and thus rendered non-available (at any rate for the time being) to the crop.[13]

It has been suggested that, in presence of undecomposed organic matter, the added nitrate may undergo denitrification in the swamp soil. Nitrogen in elementary form may be lost either through spontaneous decomposition (photochemical or otherwise) or through interaction of nitrites with the amino-bodies that may be present in the soil systems. The extents to which the different types of changes contribute to loss of nitrogen have not yet been assessed. In this connection, attention may be drawn to the work of Fowler and Kotwal[14] who adduced evidence to show that loss of nitrogen through purely chemical changes is negligible.

Most workers[15] are agreed that nitrates should not be applied to the swamp soil in the early stages. At a later period, however, and especially just prior to flowering, the crop responds well to nitrates and increased yields have been reported.

Nitrogen transformations attendant on the decomposition of different organic substances has been studied by a few workers.[16] It has been found that substances with narrow C-N ratios are ordinarily decomposed, rapidly yielding considerable quantities of ammonia. Only small quantities of nitrates are formed. There is also significant loss of total nitrogen. This loss is mostly traceable to volatilisation of ammonia. Similar changes, though less pronounced, occur also under dry soil conditions.[17]

Volatilisation of ammonia and attendant loss of nitrogen can be largely prevented by addition of substances with wide C-N ratios. Thus, addition of powdered lantana or glucose will check the loss of nitrogen from soils receiving rich dressings of urea or dried blood.

When substances with wide C-N ratios are applied, there is very little ammonification and practically no loss of total nitrogen. On the other hand, there is steady loss of carbon until a C-N ratio of about 15–1 is attained. After that stage, both carbon and nitrogen are lost, though comparatively slowly.

Volatilisation of ammonia is not probably the only means by which nitrogen may be lost from the soil system. There are probably number of other ways which have not so far been adequately understood. A great deal of further work is needed before any conclusive opinion can be expressed on the subject. The problem is one of considerable practical importance and it is hoped that, beforelong, it will be possible to organise a co-operative scheme of research (preferably under the auspices of the Imperial Council of Agricultural Research) which will not only throw fresh light on the mechanism of nitrogen loss, but will also lead to the development of new and improved methods of conserving soil nitrogen.

Except for the production of certain gaseous and water-soluble products, the transformation of organic carbon in the swamp soil have not so far been adequately studied. Thus, it will be of interest to determine the nature of the residual organic matter, the quantity left at each stage and the transformations subsequently undergone by it. Some information is available regarding water-soluble substances like cane molasses or urea which, if applied in moderate quantities, are completely decomposed and leave practically no solid residue.[18] The changes undergone by bulky organic manures, which are attacked more slowly, are awaiting elucidation.

In spite of their very great practical importance, mineral transformations in the swamp soil have not so far attracted much attention. It is only in recent years that some work has been undertaken and the available results may be summarised as follows :—There is increased availability of calcium and potassium. This is no doubt greatly facilitated by the decomposition of organic matter and consequent production of organic acids. Availability of phosphorus is also increased. Indeed, Sivan[19] has shown that ploughing in with green manure is one of the cheapest methods of increasing the availability of rock phosphates. Increasing quantities of certain metallic ions (especially ferrous iron) are also brought into solution.[20] The extent of dissolution of iron is influenced by a number of factors such as the nature of the soil, the chemical composition of the organic matter, reaction of medium, temperature, degree of submergence and such like.[21] In soils which are alkaline or contain useful quantities of lime or other buffering constituents, the iron is precipitated almost immediately after it is brought into solution. In other types of soils (especially acid ones), the iron in solution continues to persist for several weeks. The dissolved iron is present, not as bicarbonate as suggested by some earlier workers[22] but mostly as salts of organic acids. After the subsidence of the initial fermentation and on exposure to air, it undergoes hydrolysis and tends to get oxidised, with the result that iron is deposited in finely divided form as ferric hydroxide. It is this which constitutes the red-brown, fluffy layer often found at the surface of the swamp soil. In addition to this, iron is also precipitated as the carbonate, sulphide or the phosphate. The last reaction involves the removal of a part of the phosphate in solution. The precipitated phosphate is finely divided and is available, at any rate, to the immediate crop.[23]

If present in more than traces, ferrous iron in solution is toxic to plant growth. It would follow, therefore, that the soils in which the iron continues to remain in solution for long periods require some rest before the crop can be planted. On the other hand, the soils in which the iron is rapidly precipitated require very little rest and are suitable for early planting. The right stage for planting is now determined empirically, but it should be possible to develop some simple chemical methods of determining it.

The rôle of the precipitated or oxidised iron has not yet been fully worked out. Being finely divided and intimately mixed with the residual organic matter, it should be highly potent in bringing about oxidation changes and thus increasing the availability of plant food. Some useful evidence in this direction has already been obtained.[24]

The transformations of iron may be represented as follows :—

$$\underset{\text{(insoluble)}}{Fe^{\cdot\cdot\cdot}} \xrightarrow[\text{(In presence of fermentable orgnaic matter)}]{\text{Reduction}} \underset{\text{(soluble)}}{Fe^{\cdot\cdot}} \quad .. \quad (1)$$

$$\underset{\text{(in solution)}}{Fe^{\cdot\cdot}} + \begin{matrix} H_2S \\ X_2CO_3 \\ X_3PO_4 \end{matrix} \longrightarrow \begin{matrix} FeS \\ FeCO_3 \\ Fe_3(PO_4)_2 \end{matrix} \quad (2)$$

(Product of fermentation or already present in soil) (precipitate)

$$2\,Fe^{\cdot\cdot} + 3O + H_2O \longrightarrow Fe_2O_3 \times H_2O \quad (3)$$

(exposure to air) (fluffy precipitate)

$$2\,Fe_2O_3 + C \longrightarrow 4\,FeO + CO_2 \quad .. \quad (4)$$

(residual organic matter)

$$2\,FeO + O \longrightarrow Fe_2O_3 \quad .. \quad .. \quad (5)$$

(re-exposure to air)

Small quantities of aluminium are also brought into solution. It is very difficult to estimate this quantity because even with the least agitation, the dissolved aluminium passes again into insoluble condition. It is then present as an exchangeable base and can be extracted in the usual way.[25] The mechanism of dissolution and the subsequent transformations of aluminium are still awaiting elucidation.

Decomposition of organic matter also facilitates increased dissolution of manganese. At the outset, the manganese of the soil is mostly present as the dioxide, some soils containing more than others. In the reducing atmosphere of the puddled soil and in presence of the acids, the dioxide is reduced and brought into solution in the manganous condition. As in the case of iron, the quantities actually present in solution are determined by a number of factors, the most important of which is the reaction. When the fermentation subsides, manganese in solution is first precipitated and then oxidised to a hydrated oxide. The latter is highly reactive and facilitates subsequent oxidation changes in the soil.[26]

The transformations of manganese and their bearing on the nutrition of the rice plant have not yet been fully worked out. Further work in this direction will lead to highly fruitful results.

Another interesting change, attendant on swamping, is the increased availability of silicon. Application of organic manures (especially green manure) further improves the availability. Since the rice plant (especially the straw and the husk) is exceptionally rich in silicon, the increased availability of this element may, at any rate, partly account for the beneficial effect of swamping.[27]

The mechanism of dissolution of silicon has not, so far, been fully understood. It may be mentioned, however, that soluble silicates (which behave in the same manner as colloidal silica) increase the availability of phosphorus. This aspect of the problem has been studied by a number of workers, but the more recent work of Sreenivasan[28] would suggest that silicon acts by combining preferentially with the soil complex and thus releasing phosphorus for the plant. Fermentation of organic matter releases phosphorus and thus produces an effect which is somewhat *similar to that of light dressings* of alkali silicate.[29]

One of the most striking features about the cultivation of rice is the enormous demand for water. All the superior varieties of rice and, even many of the coarser ones, flourish best only under the conditions of the swamp soil. The crop, by itself, takes very little water—at any rate, no more than most other dry cultivated crops do.[30] It is, nevertheless, a common experience that if the water supply is reduced or the crop raised under conditions of dry cultivation, growth is adversely affected and yield considerably lowered. The available evidence would suggest that swamp soil conditions provide certain constituents which are not, ordinarily, readily available in the dry soil. One of these is silicon, but there are probably great many others which are essential to the rice plant and are released only under the conditions of the swamp soil. If the nature of these substances can be determined, it may be possible to provide them in comparatively stable forms even under dry soil conditions and thus improve the yield of rice. Intense research in this direction will lead to findings of very great practical value.

[1] Fowler and Deo, *J. Ind. Inst. Sci.*, 1921, **4**, 149.

[2] Sen, *Agri. J. India*, 1929, **24**, 229.

[3] De, *Ind. J. Agric. Sci.*, 1936, **6**, 1237.

[4] Sreenivasan and Subrahmanyan, *Proc. Ind. Acad. Sci.*, 1934, **1**, 123.

[5] Oelsner, *Centrabl. Fur. Bakt.*, 1917–18, **II**, **48**, 210. *k*

[6] Subrahmanyan, *J. Agric. Sci.*, 1927, **17**, 429.

[7] Subrahmanyan, *ibid.*, 449.

[8] Subrahmanyan, 1927, *loc. cit.*

[9] Subrahmanyan, *J. Agric. Sci.*, 1929, **19**, 627.

[10] Harrison and Aiyer, *Mem. Dept. Agric. India*, 1913, **3**, 65; 1914, **4**, 1; 1916, **4**, 135; 1916, **5**, 1; Harrison, *ibid.*, 1920, **5**, 181; Aiyer, *ibid.*, 1920, **5**, 173.

[11] Subrahmanyan, 1929, *loc. cit.*; Bhaskaran, Narasimhamurthy, Subrahmanyan and Sundara Iyengar, *Proc. Ind. Acad. Sci.*, 1934, **1**, 155.

[12] Nagaoka, *Bull. Tokyo Coll. Agric.*, 1904–05, **6**, 285; Daikuhara and Imasaki, *Bull. Imp. Agric. Sta., Japan*, 1907, **1**(2), 7; Kelly, *Hawaii Agric. Expt. Sta. Bull.*, 1911, No. 24.

[13] Subrahmanyan, 1929, *loc. cit.*

[14] *J. Ind. Inst. Sci.*, 1924, **1**, 29.

[15] Kellner, *Landw. Versuchstat*, 1884, **30**; Nagaoka, *Bull. Coll. Agric. Tokyo*, 1904, **5**; Kelly, *Hawaii Agric. Expt. Sta. Bull.*, 1911, No. 24; 1914, No. 31; Dastur and Malkani, *Ind. J. Agric. Sci.*, 1933, **3**, 157.

[16] Harrison, *J. Bd. Agric. Brit. Guiana*, 1912, **61**, 71; Itano and Arakawa, *Ber. Ohara Inst.*, 1927, **3**, 331; Osugi, Yoshie and Komatsubara, *Mem. Coll. Agric. Kyoto*, 1931, **12**, 1; Sreenivasan and Subrahmanyan, *J. Agric. Sci.*, 1935, **25**, 6.

[17] Sreenivasan and Subrahmanyan, 1935, *loc. cit.*

[18] Sreenivasan and Subrahmanyan, 1935, *loc. cit.*; Narasimhamurthy and Subrahmanyan, *Proc. Ind. Acad. Sci.*, 1935, **1**, 823.

[19] *Mem. Dept. Agric. Ind. Chem. Ser.*, 1925, **7**, 145.

[20] Bhaskaran *et al.*, *loc. cit.*

[21] Sundara Iyengar and Subrahmanyan, *Proc. Ind. Acad. Sci.*, 1935, **1**, 868.

[22] Robinson, *Soil Sci.*, 1930, **30**, 197.

[23] Sreenivasan and Sadasivan, unpublished data.

[24] Harihara Iyer, Rajagopalan and Subrahmanyan, *Proc. Ind. Acad. Sci.*, 1934, **1**, 106; *ibid.*, 1935, **2**, 108.

[25] Govindarajan, unpublished data.

[26] Harihara Iyer, Rajagopalan and Subrahmanyan, *loc. cit.*; Rajagopalan, unpublished data.

[27] Nanji and Shaw, *J. Soc. Chem. Ind.*, 1925, **44**, 1 T; Sreenivasan, *Curr. Sci.*, 1934, **3**, 193.

[28] *Proc. Ind. Acad. Sci.*, 1935, **1B**, 607; **2B**, 201; 1936, **3B**, 283, 302.

[29] Sreenivasan, *Proc. Ind. Acad. Sci.*, 1936, **3B**, 258.

[30] Briggs and Shantz, *J. Agric. Res.*, 1914, **3**, 1; Leather, *Mem. Dept. Agric. Ind. Chem. Ser.*, 1911, **1**, 10; B. N. Singh, R. B. Singh and K. Singh, *Proc. Ind. Acad. Sci.*, 1935, **1**, 471.

RESEARCH ITEMS.

Boundary Problem in a Non-Linear Partial Differential Equation of the Fourth Order.—Considering the non-linear partial differential equation $\frac{\partial^4 u}{\partial x^4} + \frac{\partial^2 u}{\partial t^2} = p(x, t)u^3$ in the domain $0 \leqslant x \leqslant \pi$, $0 \leqslant t \leqslant T$, the problem is to find its regular solution $u(x, t)$ satisfying the conditions

$$u(0, t) = u(\pi, t) = 0 \text{ in } 0 \leqslant t \leqslant T,$$

$$u(x, 0) = f_1(x), \frac{\partial u}{\partial t}(x, 0) = f_2(x) \text{ in } 0 \leqslant x \leqslant \pi.$$

This has been considered by M. R. Siddiqui (*Ind. Physico-Math. J.*, 1937, **8**) and it is found that for a restricted T, one and only one solution exists which can be expressed as a Fourier series $u(x, t) = \sum_n v_n(t) \sin nx$, wherein the coefficients $v_n(t)$ are determined with the help of an infinite system of non-linear integral equations, which is solved by the method of successive approximations.

Amphoteric ion.—A review of considerable interest has recently been published (P. Rumph, 'La Theorde de L'ion Amphotere,' *Actualites Scientifiques et Industrielles*, 1936, No. 374). The review covering just 50 pages is divided into three chapters: (1) the existence of amphoteric ions, (ii) the dielectric constants of aqueous solutions containing amphoteric ions, (iii) calculation of the different dissociation constants and the relationship between the activities of the amphoteric ions and those of the uncharged molecules.

In a brief conclusion, the author draws attention to the usefulness of this concept of amphoteric ions in branches of chemistry other than a pure study of biological substances, such as, in the theory of colouring matters, the constitution of complex compounds of inorganic salts, etc.

Histology of the Skin of *Protopterus*.—The African lung-fish, *Protopterus annectens*, is known