

Soils and Fertilisers*

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MANY of the investigations in agricultural chemistry during the past half-century have been concerned with the more accurate and detailed working out of the ideas discussed by Gilbert in his presidential address to the Chemistry Section of the British Association in 1880 and with the explanation of various points in agricultural practice which have been evolved by farmers; while nothing spectacular in the way of change may have resulted, the cumulative effect of the more accurate knowledge about soils, fertilisers, crops and nutrition has undoubtedly been important.

In addition, several discoveries of fundamental importance have been made: the synthetic manufacture of ammonia and nitrates; the effects of vitamins in animal nutrition; the theory of base exchange in soils; and the development of bacteriology, to mention some of the more outstanding only.

Some of these, although they might be described as advances purely from the scientific side, have yet had practical applications of the highest importance. The theory of base exchange in soils, which may be said to have originated in Great Britain with the early work of Way in the fifties of last century and is associated in modern times with the names of Gedroiz, Hissink and Wiegner, has provided an explanation of absorption and exchange phenomena and of soil acidity, and has been successfully applied to the reclamation of alkali soils in Hungary (Von Sigmund) and the western States of America, as well as in the treatment of land recovered from the sea.

Amongst other notable advances which have had a practical application may also be mentioned the use of sulphur for reducing fungoid attacks on crops and for reducing alkalinity in soils, particularly soils used for growing potatoes, and the study of the functions of elements which occur only in minute quantities in plants, for example, copper, manganese and boron. The application of modern statistical methods to the interpretation of field experiments and of biological experiments generally, has led to a more accurate appreciation of the experimental errors involved, and of the significance attached to any result.

THE SOIL

The study of the soil may be approached from two points of view. In the first of these it is regarded as the seat of certain chemical, physical and biological processes which are investigated entirely from the scientific point of view without any reference to agriculture. This has been the

method of attack of the Russian school in particular, and the supposition is that when a sufficient body of knowledge has been accumulated in this way, the consideration of the facts obtained may result in practical applications of value to the agriculturist; it should be emphasised, however, that the approach in the first instance is purely scientific. The interesting volume published a few months ago by Prof. G. W. Robinson of Bangor gives a clear exposition of the methods of this school and of the results which have, so far, been obtained. The other method has been to study the soil as the medium of plant growth, to investigate practical problems as they arise and to have as its definite aim the giving of advice to those engaged in agriculture as to improving their methods of tillage and crop production. It is obvious, of course, that no definite division can be made between the two methods of approach, as is shown by the history of recent developments. In Great Britain, while the former method has been by no means neglected, as witness the large amount of research work carried on at Rothamsted and to a lesser degree elsewhere, it is the latter method which has been in the main officially supported and subsidised by successive Governments.

Amongst the scientific methods which have emerged and received considerable prominence and support in recent years is the modern method of soil classification. This, while belonging to the scientific method of investigation, also seeks to justify its existence by the claim that it is of immediate importance to the farmer. The method was first developed in Russia, where it was shown as early as 1879 that climate is responsible for the great tracts of similar soil found in that country; this idea was developed by later workers and more recently by Glinka and others, who recognised some of the limitations of the original method and proposed in place of the earlier zonal type of classification a system based on the effect of climate on the development of the soil profile. Soils were divided into two great groups. In the first were placed the soils in which the profile shows that the external soil-forming processes, especially climate, have predominated; the second group comprises those soils in which the internal process, that is, parent material, still predominates. These groups are further subdivided, but the whole system lays special emphasis on the development of the soil profile—that is, the vertical section from the surface soil to the unweathered parent material.

Although soil surveys had been carried out for a considerable time in Europe and the United States, modern soil-surveying may be said to date from the first International Soil Congress held at Budapest in 1909. At this meeting Glinka explained the new method of classifying and mapping

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soils on a climatic basis, and soil surveys on the new basis were soon begun in a large number of European countries and in the United States. At the International Soil Congress held at Rome in 1924 it was agreed to construct a soil map of Europe, and in 1926 the special committee representative of the different countries concerned met in Hungary to discuss in the field the practical details of the work on which the map was to be based. At a subsequent meeting in Budapest the details of the methods were adjusted, and it was agreed to undertake the construction of a map of the soils of Europe based on as uniform a method of surveying as possible. The "General Map of the Soils of Europe", under the editorship of Prof. Stremme, Danzig, was published in 1927. The English text, translated by Dr. W. G. Ogg, of the Macaulay Institute for Soil Research, Aberdeen, was published in 1929 with the aid of a grant from the Department of Agriculture for Scotland. The first edition of the map is on the scale of 1:10,000,000, and preparations for a second edition are in progress.

Turning next to the methods employed in surveying, the profile is studied as regards horizons, colour and texture changes, structure, drainage and vegetation. The surface horizons are naturally more extensively studied. As regards the chemistry of the profile, most weight is placed on the ratio of silica to sesquioxides; other factors examined are the presence and accumulation of salts, including calcium carbonate, and changes in acidity with depth. On the results of these observations, the soil is placed in its appropriate class. In passing, it may be noted that there appears to be a certain reluctance on the part of the advocates of these methods to ascertain by means of carefully conducted field experiments whether some of the differences they are mapping are really significant in practice and whether some of the finer differences which they map, between soils within the same type, have any reality and make any appreciable difference in agricultural practice.

As regards the utility of soil surveys generally, a reasonable case can be made out for the benefits which are likely to follow a careful survey of a new country which is just being developed. The difficulty there, is to provide the staff and funds so that the survey work is kept ahead of the development.

In a country like Great Britain, on the other hand, there is doubt on the part of many as to whether the benefits which are supposed to follow such a survey will ever be realised. The question of suitable crop distribution and association is well established, as the result of generations of experience and is not likely to be seriously altered as the result of such an investigation. It is claimed that a soil survey on the scale of 1 inch to the mile would be of great importance in connexion with manuring and in the interpretation of the results obtained by the various methods of estimating the available plant nutrients in the soil. Before undertaking a survey of such magnitude, it

should be pointed out that such a claim would require to be based on the results of a wider series of accurate field trials than are available at present. At the same time, the importance of survey methods from the purely scientific point of view and also in connexion with land reclamation problems should not be overlooked.

What the farmer wishes to know about the soil is whether it is adequately supplied with nitrogen, phosphates and potash, and whether there is sufficient lime present to give a satisfactory soil reaction. These are reasonable questions, but it must be admitted that in the past the task of the agricultural chemist who had to attempt to answer them was by no means easy.

With regard to nitrogen, no method exists by which we can judge the requirements of a soil as regards this element; the fact that most soils respond to dressings of soluble nitrogenous fertilisers is about as far as we can go in the way of prediction.

On the other hand, the lime requirement of a soil can now be given with reasonable accuracy by routine methods which are suitable for use on a large scale. The question as to whether the dressing of lime which is theoretically desirable can be recommended is generally an economic rather than a chemical one.

To determine what the requirements of a soil are with regard to available phosphates and potassium is a more difficult matter. The most that can be aimed at at present is to be able to say whether the soil is well supplied or moderately supplied with these constituents, or is deficient in them.

The difficulties of discriminating between the available and non-available constituents in a soil are obvious. In the first place, the way in which plants take up their nutrients from the soil is still a matter of controversy, and the fact that the soil is a heterogeneous and ever-changing system of extreme complexity greatly increases the difficulties. The chemical methods generally employed involve the extraction of the soil with water or some dilute solvent and the estimation of the phosphates and potassium which come into solution under standard conditions. When the results can be interpreted in the light of field experiments or experience, they are a very useful guide in advisory work. The fact that the method is an empirical one is a great drawback, but the more serious objection is that the results give a measure of the condition of a soil at a particular time only and obviously cannot apply to its condition at different times throughout the year. There is probably no hard and fast line between the 'non-available' and the 'available' constituents, the one set gradually merging into the other.

These fundamental difficulties have suggested the idea of making use of the plant itself as an index to the available plant nutrients in the soil. Much work from this point of view has been carried out and two methods based on these principles have been in use on the Continent for

several years. These are the well-known methods of Mitscherlich and Neubauer. These methods have been very ably and critically reviewed by Dr. R. Stewart in a recent publication of the Imperial Bureau of Soil Science (*Technical Communication* No. 25, 1932).

One general difficulty which applies to both methods is that they can be carried out only at institutes specially equipped for the purpose. The Mitscherlich method requires a whole season to carry out the test, while the Neubauer requires much supervision and extreme accuracy in the analytical work. Attempts have therefore been made to devise simpler biochemical methods suitable for the ordinary laboratory use; of these one is of special interest.

The Aspergillus Method. It is found that under standard conditions the growth of *Aspergillus niger* is proportional to the amounts of available potash and phosphates in the soil.

The mould is grown in a suspension of the soil in a culture solution containing all the constituents necessary for growth except the one being tested for, and the results of a large number of experiments have shown that the standard error is of the order 4 per cent.

The method has been worked out by Prof. Niklas and his colleagues at the Agricultural Research Station at Weihenstephen, near Munich, and has also been subjected to a critical examination by Dr. A. M. Smith, Edinburgh, who has tested the method with a variety of Scottish soils, as well as investigating the effect of different sources of nitrogen on the process.

The *Aspergillus* method is likely to be valuable in estimating the potassium and phosphate requirements of a soil. The results, as might be expected, are more reliable for potassium than for phosphates, and while not rigidly quantitative, give information as to whether the soil is rich or poor in these constituents. It has the advantage of being rapid and requiring no expensive apparatus (A. M. Smith and R. Coull, *Scot. J. Agric.*, vol. 15, p. 262; 1932).

The whole question of available plant food is necessarily bound up with the complex relationships which exist between plant and soil, and it is unlikely that any simple or single method will be devised to overcome the inherent difficulties of the problem and be generally applicable to different sets of conditions. The admitted lack of agreement obtained with the various methods at present in use is undoubtedly due, to a large extent, to the variety of factors involved, as well as to the fundamental objections which may be raised to any one method. We are still very ignorant of the process of assimilation by the growing plant, and until we have more information on this subject, methods of estimating availability must continue to be largely empirical and the results merely first approximations.

The usual method of approach to the problem has been to study the effect of the soil or plant medium on the plant. In Edinburgh attention

has in recent years been directed in the opposite direction—namely, to a study of the effect of the plant on the soil. The alterations to be observed are, of course, small, but by applying methods which might almost be described as analogous to modern micro-methods of analysis, measurable changes can be followed with considerable accuracy. The results which have been obtained are interesting and sometimes rather unexpected, and although it is scarcely to be supposed that they will furnish a complete picture of the relationship between soil and plants, one feels that any contribution to the subject from a new angle may be of value in the study of such a complex problem.

FERTILISERS

Turning next to the progress which has been made in the manufacture and use of fertilisers since the time of Gilbert's address, there are one or two notable dates and achievements to be mentioned.

First in order of time is the discovery of the value of basic slag as a fertiliser. The earliest experiments with slag in this country were carried out in England by Wrightson and Munro in 1885, and by A. P. Aitken in Scotland about the same time; a year or two later J. J. Dobbie carried out the first experiments with the slag in North Wales.

The now classic experiments laid down by Prof. Somerville in 1896 and carried on and developed by his successors, Sir Thomas Middleton and Prof. Gilchrist, have demonstrated the value of this addition to phosphatic fertilisers and show as the result of twenty-five years' experiments that basic slag is, for certain types of soil, even more valuable than superphosphate.

As regards superphosphate, it should be noted that the former view, that it was an acid manure and that its continued use depleted the soil of lime, is no longer held; the general objection to the use of the so-called physiologically acid manures has been shown to be due to misconceptions as to their action.

In the case of the potash fertilisers, one of the most striking discoveries of recent years is the marked response of most fruits to potash manuring; the effect of potash salts on the quality of the crop, particularly in the case of potatoes and barley, has also received considerable attention.

The most important advance of all is the manufacture of nitrogenous fertilisers by synthetic methods from the nitrogen of the air. Ammonia is now manufactured by a synthetic method on an enormous scale at the works of the Imperial Chemical Industries, Ltd., at Billingham. The successful development of the method is one of the greatest triumphs of chemistry and engineering in modern times. By this process, which incidentally dispenses with the use of sulphuric acid, sulphate of ammonia can now be prepared more cheaply than from gas liquor where the ammonia is obtained as a by-product.

Concentrated Complete Fertilisers. One of the most interesting developments of the synthetic ammonia industry has been the manufacture of concentrated complete fertilisers containing nitrogen, phosphates and potash in suitable proportions and all soluble in water. One ton of such fertilisers supplies as much plant food as two tons of the ordinary mixed fertiliser of similar composition. They possess the obvious advantage of reducing freight and handling charges and cost of distribution to the land; they are granular in texture and very easy to sow, and they can be stored without risk of deterioration; further, the constituents are all soluble in water.

Another point claimed in their favour is that

they contain little except the three fertilisers, nitrogen, phosphates and potash, while the ordinary fertilisers contain appreciable, and in some cases large, amounts of calcium, sulphur and other elements. It is possible that in some soils the absence of the additional substances might be a disadvantage, and a careful comparison of the new fertilisers with the old mixed fertilisers will be necessary to show that no disadvantage attends the use of the new compounds over a number of years.

It is obvious that if the concentrated fertilisers were used continuously over a number of years, increased attention would require to be given to liming.

Inter-Atomic Distances and Forces

ON September 11, in Section B (Chemistry) of the British Association meeting at Leicester, Dr. N. V. Sidgwick opened a discussion on "Inter-Atomic Distances and Forces in Molecules", with a review of the methods available for the determination of interatomic forces and distances.

X-Ray Measurements. Since the wave-length of X-rays is of the same order as atomic distances, scattering of these rays gives information about the relative positions of atoms. This method of investigation has been applied extensively to solids, especially by Sir William and W. L. Bragg ever since its original suggestion by Laue, and has been extended more recently by Debye and others to liquids and vapours, where deformation of the molecules by crystal forces is absent. The method has been supplemented by use of electron waves.

Optical and Infra-red Spectra. Electronic energy changes correspond to spectral lines in the visible or ultra-violet region, but oscillation of molecules causes absorption of energy in quanta represented by lines in the infra-red. These differences may be imposed upon electronic changes to give the lines of a band spectrum. Rotational frequencies give lines in the far infra-red which, when imposed upon electronic and vibrational changes, give the fine structure lines of band spectra. From rotational quanta the moment of inertia of the molecules can be calculated; hence with known masses, inter-atomic distances and ultimately valency angles can be found. Oscillation frequencies indicate resistance to deformation of links.

Thermochemical Data. The energy given out when two atoms form a link is connected with the force constant of the link derived from its oscillation quanta; these are connected, however, with small changes only in the energy of the link, while the heat of formation represents the total energy associated with the link.

Dipole moments. These are produced whenever two unlike atoms form a link, and are due to unsymmetrical sharing of electrons. As resultant moments are obtained by compounding the simple vectors, observational values give indications of the valency angles. The values vary with the

nature of the atoms, and with the nature and number of the links between them.

The properties of a link depend upon whether it is ionised or covalent, and, if covalent, upon whether it is single, double or treble. It is important to be able to distinguish the different kinds of links, and light has been thrown upon this by wave-mechanics. Measures of the lengths of covalent links accurate to about five per cent are now available and can be assigned in molecular structure. A double link is shorter than a single, and a triple link shorter than a double link between corresponding atoms. When, however, no link is present, atoms cannot approach so near to one another owing to electron repulsion. Atomic centres in the hydrogen molecule H_2 are 0.75 A. apart, but uncombined hydrogen atoms cannot normally approach within less than 2 A. of each other. In methylene chloride there is room for the chlorine atoms if the $C \begin{matrix} \diagup \\ \diagdown \end{matrix} Cl$ angle is the tetrahedral one, but the 'envelopes' interfere causing separation of the chlorine atoms. This is obviously important in questions of steric hindrance.

The theories which have been put forward to explain the covalent link were reviewed by Prof. J. E. Lennard-Jones. In 1927 Heitler and London applied new physical methods to the investigation of chemical linkages. The reactions of atoms to light indicate the energy states of the atoms. There is a natural tendency for a system to revert to its lowest energy state. Heitler and London considered that atoms were each in the lowest ground state when reacting; certain pairings of electron spins were thus possible, but the theory failed to explain either directed valencies or double bonds. Pauling and Slater suggested that it was necessary to consider other states of an atom when a second atom was near. Thus in carbon, two 2_s and two 2_p electrons were replaced by one 2_s and three 2_p electrons, enabling four shared pairs of electrons to be made up. The definite orbits of the Bohr atom are thus diffused by the merging of the neighbouring energy levels, and the superimposing of the four necessary orbits