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CLAY MINERALS

By

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Introduction

Fundamental studies on the mineralogy of the clay fraction in soils were initiated in the Chemistry Department at Rothamsted shortly before the war. With the outbreak of war the work largely ceased, and it was not resumed until A. Muir came in 1945 from the Macaulay Institute for Soil Research to start the Pedology Department. The work carried on since the war falls naturally into two parts, which will be considered separately. The first is the study of mineralogy of clays * and the second the study of their properties.

Mineralogy of Clays

Introduction

To define a mineral we must know its composition and either its structure or some properties which are related to its structure. The vast body of mineralogy was built up before methods of determining structure existed, and such properties as refractive indices, birefringence, shape of crystals and hardness were used to define structural types. With minerals which form visible crystals there is no difficulty in finding their composition, for almost pure samples can be separated. With the clay minerals, which for the most part exist as crystals less than 1μ in diameter, isolation of pure materials is not easy, and the structural properties which can be obtained with light microscopes were often determined on impure materials.

With the advent of X-ray diffraction a direct method of determining atomic arrangement in crystals, that is their structure, became available, and has been applied with success to a large number of mineral structures. The information obtained from X-ray-diffraction spectra is of two kinds; the geometrical distribution of reflections is a measure of the geometry of atomic planes in the crystal, in particular their interplanar spacings and interplanar angles; the intensities of the reflections are related to the arrangement of atoms in the planes. With a single-crystal specimen, spacings, angles and intensities can be measured. With fine-grained materials such as clays we cannot obtain single crystals large enough to handle, and powder specimens, which are really aggregates of more or less randomly oriented small crystals, must be used. From patterns obtained with powders we can, in theory, obtain interplanar spacings and intensities of reflections; but we can derive little information from them about interplanar angles, and hence complete structure determinations are not possible except with the simplest structures. With complex structures the reflections from different sets of planes overlap, so that the information obtainable

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* For a recent review of this subject see G. W. Brindley (1951). *X-ray identification and crystal structures of clay minerals.* (London: Mineralogical Society.)

from powder patterns is limited. However, structure determinations on minerals such as micas which are similar to the clay minerals, but which form larger crystals, led to a realization of the principles which appear to govern the structures of such materials. Information on the co-ordination of cations and what kind of isomorphous substitutions could occur became available, and by comparing X-ray powder patterns of well-crystallized layer silicates with those of clays, the broad outlines of the structures of the different groups of clay minerals have been obtained.

Knowledge of the structures of clay minerals gives a method of determining the purity of a clay mineral sample by comparing the observed X-ray-diffraction pattern with that expected from a particular structure. In this way, from information on the chemical composition and X-ray patterns of apparently mono-mineralic clays, a body of knowledge has been built up which enables the different clay mineral groups which are present in a mixture to be recognized.

The majority of clay minerals have layer structures consisting of parallel layers containing Si, Al, O and OH and sometimes Mg, Fe and other elements. The layers consist of parallel sheets of atoms which are firmly bound together so that the layers are fairly stable; between layers the forces are usually weaker. Thus sheets of atoms are bound together to form layers, and layers are superposed to form crystals. The classification of the clay minerals is largely based on structural considerations, for the compositional range within groups is of the same order as between groups.

In the structural field there are essentially two main types of layer which form clay mineral crystals. First, there is the type of layer found in minerals of the kaolin group, which is often called a 1 : 1 layer, as it is made up by the condensation of one sheet of tetrahedrally co-ordinated cations with one sheet of octahedrally co-ordinated cations. The thickness or height of a single 1 : 1 layer is about 7·2 Å. The other type of layer, which is the basic layer of micas, chlorites, vermiculites and the montmorillonite minerals, is the 2 : 1 type, for it is made up by the condensation of two tetrahedrally co-ordinated sheets of cations, one on either side of an octahedrally co-ordinated sheet. The thickness of a single 2 : 1 layer is about 9·3 Å. In a broad way we cay say that 1 : 1 type layers are electrically neutral in themselves. The 2 : 1 layers often carry a negative charge due to isomorphous substitutions, and these negative charges are balanced by positively charged atoms or groups of atoms which are intercalated between successive 2 : 1 layers. This leads to the range of minerals made up of 2 : 1 layers, for both the size of the negative charge per unit volume of layer and also the nature of the balancing positive group can change. Thus the layer height for the minerals composed of 2 : 1 layers depends on the size of the positively charged interlayer group. In the micas K^+ ions balance the charge on the 2 : 1 layers and the thickness of a mica layer is about 10 Å., in the vermiculites moderately hydrated cations are found between the 2 : 1 layers and the height of a vermiculite layer is about 14 Å., and in the montmorillonite minerals the balancing cations are even more highly hydrated and the layer height depends on the precise nature of the cation and the humidity. It is chiefly on the basis of these different layer thicknesses that the clay minerals in mixtures are recognized by X-ray methods; the X-ray-

diffraction pattern, since it measures the distance between similar planes of atoms, gives a direct measure of the height of the layers.

Soil clays

The work of this department in connection with soil clays can be divided into three parts. First and most important, for all else depends on it, has been the improvement of methods of obtaining X-ray-diffraction patterns, then development of methods of interpreting some of the complex diffraction patterns obtained and finally investigation of the best ways of applying these methods to the study of soil genesis.

The chief method used to identify soil clays is by X-ray-diffraction patterns, and until recently it was frequently suggested that amorphous material, including organic matter, in soil clays interfered with the diffraction patterns. Various chemical methods have been used to remove the amorphous inorganic material by solution, and organic matter by oxidation and solution. In some cases it appears that the composition of the crystalline clay fraction is altered by these treatments. In the work in this department on soil clays from many different parts of the world, we have found that the cleaning of clays is not necessary in order to obtain good, clear diffraction patterns. The reflections may not always be sharp; but in such cases the broad reflections are due to the nature of the material, which is often imperfectly crystallized. It appears that the use of cleaning techniques arose out of poor X-ray technique and that if proper attention is given to features such as clean radiation and good collimation, diffraction patterns with clear reflections will generally be obtained. This must not be taken as a suggestion that " amorphous " matter does not exist in soils or even that it is rare; but when it is present it is better to examine the specimen before treatments are applied to remove the poorly crystallized fraction. It would seem desirable to disperse soil clays using the mildest possible reagent, and then the results apply more directly to clays as they exist in the field. Having examined the clay as it is in the soil, we can apply cleaning treatments and relate their effects to what was present in the untreated clays.

Examination of soil clays from England, using mild dispersion treatments, has shown the presence of the hydrated iron oxide, lepidocrocite, in many soils which show the orange mottling characteristic of impeded drainage. Had the clays been treated to remove amorphous matter, the form of the iron oxide would have been left unknown, and it is suspected that failure to detect lepidocrocite earlier and more frequently is due to treatments to " purify " the clay minerals.

In connection with the interpretation of X-ray-diffraction patterns of clays, work has been done on interstratified clay minerals. It was pointed out in the introduction that slight variations in the interlayer grouping have different layer heights characteristic of different minerals. Usually, individual crystallites are composed of only one type of layer of a characteristic thickness, and a sample may be composed of a mechanical mixture of two kinds of crystallites, one with say 10 Å. layers, i.e., mica, and another with 14 Å. layers, i.e., vermiculite. However, in some cases within a single crystallite both 10 Å. and 14 Å. layers occur. These layers may be

arranged in a regular way with respect to each other, or they may be randomly distributed within the crystallite, and the interpretation of the diffraction effects from randomly interstratified systems has formed part of our work. The first step was to apply the formulae developed by Hendricks and Teller to the calculation of the patterns which would be given by a number of two-component systems which were likely to occur in soil clays. This involves several rather tedious calculations for each system, since different patterns are given by different proportions of the two components. X-ray patterns of randomly interstratified minerals are then interpreted on the basis of the best fit between the observed and calculated patterns. A detailed study has been made of an artificially prepared randomly interstratified two-component system in which some control over the proportions of each component could be exercised. The good agreement obtained between calculated and observed patterns of a range of proportions showed that the theoretical treatment was essentially correct. All the above required laborious calculations, and more recently a modified Fourier transform method has been proposed which gives the types of layer present, their proportions and their relative distributions. It also has the advantage that it can be used for systems with more than two components, although in such cases ordinary transform methods would be preferable. The transform method has been applied with success to montmorillonite–water systems.

Having established methods for taking and interpreting X-ray-diffraction patterns of clays, one of the questions arising is how best to apply our methods to the study of soil genesis. In the mineralogical field we are interested in how minerals in the soil parent material alter to give other minerals under the soil-forming processes; in particular, how rock minerals alter to clay minerals and how one clay mineral alters into another. Apart from the fact that the products of weathering form the major part of the soil, the way in which minerals break down influences the composition of the soil solution from which plants extract their nutrients.

In the past, alteration studies of clay minerals in soils have usually been made over a wide geographical range or on soils with well-developed horizons or a combination of both. The wider the spacial range covered by the study and the longer time interval from the beginning of the alteration, the greater the number of variable soil-forming factors and the greater the variation in individual factors. The results obtained from such studies can only give a time-average of all the processes which have been effective. It is obvious that soil profiles do not form initially in horizons; in fact, soil horizons are an idealization. It is rare for a soil horizon to appear homogeneous even to the unaided eye, and alteration processes occur on an infinitely more minute scale. When the soil-forming processes act on the parent material the reactions begin at points of weakness in the parent material and initial alteration is localized around such points. If there are several processes operating with different rates, we may be able to find zones with different degrees or types of alteration around active centres, and ideally we should be able to obtain information about the many processes which contribute to the end-product.

To approach the ideal of studying a single reaction, an effort is

being made to study alteration in and around small areas in the soil matrix where differences are visible. This method has several other advantages; it employs more fully the X-ray technique, which only requires small samples, it makes use of natural concentrations and so allows ready detection of minerals which are present in small amounts in the total soil and which can easily be overlooked in bulk-horizon samples. In addition, readily visible morphological features are among the criteria on which soils are classified in the field, and the information obtained will apply directly to such features. It is hoped that such studies will throw light on incipient changes and intermediate alteration stages, for the time required to develop a small feature is greatly less than that required to form an horizon, and the distance between reacted and unreacted material is small, so that constant parent material can more justly be assumed.

A preliminary study of some poorly-drained soils from Lancashire somewhat along these lines has affirmed the evidence of an earlier, broader study that lepidocrocite is an important pigment in the orange-coloured mottles associated with impeded drainage. In addition, the study showed that in these soils the clay mineral in the soil matrix in which the mottles are found were, as far as could be detected, similar in kind and amount to the clay minerals in the mottles. This evidence suggests that the iron moved into the mottled area from wherever it was released by iron-bearing minerals; for if the iron oxide in the mottles had been due to local concentrations of iron-bearing minerals in the parent material, then their alteration products would be expected to have some effect on the clay-mineral composition of the mottles.

The broader studies on a horizon basis are valuable, but for information about a particular reaction we need to use more detailed methods, for the results of broader studies are intractable to anything but a general analysis in terms of particular reactions. The method we are trying to use tends much more towards the study of a single reaction, whereas the bulk-horizon method gives the result of a set of frequently associated, but largely unknown, processes.

PROPERTIES OF CLAY MINERALS

Introduction

Clay minerals are by definition minerals of high specific surface, and the part they play in soils is largely dominated by this fact. A study of the properties of clays therefore resolves itself into a study of their surface chemistry. The main objective of such work has been to relate the mineralogy of clays to their properties with the twofold result of being able to devise new tests to identify minerals and predict the properties of clays found in soils from a mineralogical analysis.

Expanding minerals

A superficial glance at the literature on clay minerals will quickly suggest that as a class of surface-active solids they are often rather unusual. There is, for example, a marked decrease in the surface areas available to non-polar substances, such as nitrogen and benzene, and that available to polar substances, such as water or pyridine. This has been traced to the entrance of the latter class of

compound, not only into clay aggregates, but also into the clay crystallites themselves. The latter process often occurs in a regular way, so regular that it is possible to investigate the swelling of the crystallites by the changing of the positions of X-ray reflections without any loss in their sharpness. This remarkable property has enabled the arrangement of the intercalated molecules to be studied, work that was first carried out by Hendricks in 1941. This aspect has received much attention at Rothamsted, several hundred organic complexes of a wide variety of chain and ring compounds having been investigated in recent years. A survey of the results shows that molecules that can behave as cations are strongly sorbed, whilst those that tend to be anions are weakly attracted. Among the " neutral " aliphatic compounds, those that are small and highly polar, such as methanol, are favoured, but in the aromatic series additional factors, due to distribution of the charge in the molecule and molecular polarizability, assume great importance. Since the internal surface may comprise up to 90 per cent of the total surface, these studies of the interaction of the internal surface with organic compounds are important in appreciating the classes of compound that interact strongly with soil clays.

Similar methods of study have been applied to the interaction of water and expanding clay minerals, but here the information has tended to be of a different kind, namely the relation between the swelling and the external vapour pressure. At low humidities the direct method is used, whereby the clay is allowed to come to equilibrium with definite relative vapour pressures of water vapour and the swelling determined from X-ray photographs. The results indicate that there is marked hysteresis between the wetting and drying cycles, but this is reduced when the swelling is plotted, not to the relative vapour pressure, but to the amount of water taken up. Although hysteresis prevents detailed thermodynamic study of the relation between vapour pressure and uptake, it can be clearly shown that the uptake by a mineral at a given pressure is dependent on the nature of the surface cations, those of high charge and small size promoting thicker films than those of low charge and large size. This result suggests that the formation of water films on clays is analogous to the hydration of cations in solutions; the primary process of sorption being one of forming a two-dimensional water shell round the cations. Whilst recent X-ray work has confirmed that this is essentially correct, it contradicts many of the older ideas on clay–water relations, which were often based on inadequate experimental data.

Investigations of the behaviour of expanding minerals at very high humidities have also been carried out in connection with the work on clay colloids pursued in the Physics department. Here the sample may be immersed in salt solutions of known concentration or brought to equilibrium with a known water-pressure deficiency. It is found that there is generally a sharply defined limit to the swelling of the crystallites, but cases occur, for example in sodium montmorillonite, where the swelling increases reversibly with vapour pressure to an indefinite extent and the X-ray patterns indicate a progressive decrease in order as the distance between the silicate sheets increases. Clearly, when the distance between the silicate sheets is of the order of 100 Å. the system approximates to that of

a true colloid, and it should be possible to test the current theories of quantitative colloidal behaviour with the resultant experimental data. When this is done it is found that the attraction between the silicate sheets drops off much less rapidly than would be expected, and it is concluded that present theories require drastic revision where they have to deal with the behaviour of clay particles.

As the internal surface becomes thickly covered with water molecules, the interlamellar cations are more easily able to move and become available to plants. With cations of low hydration energy, however, the exchange process is slow, due to the smaller amount of water on the surface, a phenomenon which in its aggravated form is known as cation fixation, and is of considerable practical importance in the case of potassium. The principal problem in potash fixation is to understand why it is severe in some soils and absent in others, that is to say, what is the relation between fixation and the nature of the soil minerals. In answer to this question a heartening advance has recently been made, since a correlation has been found between field fixation and the presence of a 14 Å. reflection (a vermiculite mineral) on the X-ray photographs of the glycerol-saturated clay.

Another kind of cation fixation that has been investigated is that which accompanies the dehydration of a certain class of montmorillonite minerals when saturated with small cations such as lithium. This effect, which is accompanied by loss of expanding properties, is apparently due to the migration of the surface cations into the silicate sheet and the filling up of certain vacant sites. Such sites must not only be vacant but they must also be near the seat of the negative charge in the silicate sheet. These conditions define fairly closely the minerals which give this effect, and it is easy to devise a test to distinguish them from minerals in the same group which give very similar X-ray photographs. This type of test has been found useful in examining the relation between soil clays and their parent materials, as well as in classifying the numerous montmorillonite minerals in the departmental collection. Another important use of this fixation effect has been to prepare minerals with known amounts of expanding and non-expanding silicate sheets and to study the X-ray and surface effects which appear. This has a bearing not only on the surface study of the partially expanding minerals in soils, but also on the fundamental theory of X-ray diffraction applied to such problems.

Non-expanding minerals

Whilst the study of expanding clay minerals has rightly received more attention in recent years, non-expanding minerals, e.g., kaolins are also being investigated. The non-expanding minerals are not as active in soils as the expanding minerals because of their much lower specific surfaces. The methods of investigation must therefore be correspondingly more sensitive, but since hysteresis effects are absent, the theoretical treatment of the results is simplified. On the whole the effects observed have much in common with what has already been described; the surfaces are more hygroscopic if the exchange cations have a high hydration energy, and anomalous effects are observed if a small cation like lithium is present.

UPTAKE OF NUTRIENTS FROM LEAF SPRAYS BY AGRICULTURAL CROPS

By

G. N. THORNE

INTRODUCTION

Interest in the application of fertilizers in sprays has increased in recent years because of the development of concentrated highly soluble fertilizers, and because the increasing use of machinery for spraying insecticides, weed-killers, etc., and for overhead irrigation, facilitates the application of nutrients in sprays. The effects of nutrient sprays are frequently ascribed to nutrient uptake by the leaves; for example such a claim is made by Secrett (1949) to explain the beneficial results obtained from the irrigation of a cauliflower crop with water containing 1 part in 20,000 of KNO_3. In an experiment on irrigated sugar beet, in which 12 inches of irrigation water were applied during the season, the application of nitrogen in the water caused a greater increase in the yield of tops than application to the soil at sowing (Results of field experiments for 1949, Rothamsted). However, in this experiment and in Secrett's irrigations the amount of water applied was so great that most of the contained nutrient must have fallen on the soil, and not been retained by the leaves, so that the difference between solid and spray application of fertilizer was probably not due to leaf absorption, but to the sustained supply of nutrients throughout the season, resulting from the repeated irrigations. Work was started at Rothamsted in 1950 to determine whether plants can absorb appreciable quantities of nutrients from leaf sprays, and to investigate the conditions that affect the amounts so absorbed.

POT EXPERIMENTS

Pot experiments were done in which the soil was protected so that the spray could not reach the roots (Thorne, 1954). Spraying barley, Brussels sprouts, French beans, tomato and sugar beet daily for several weeks with a solution containing nitrogen, phosphorus and potassium increased the content of all three nutrients and dry weight of plants of all the species. Increase in nutrient content occurred whether nutrient supply to the roots was high or low, and was approximately proportional to the concentration of nutrient in the spray and the frequency of spraying. Previously, Lewis (1936) had found that the phosphorus content, but not the nitrogen or potassium contents, of lettuces growing in a phosphorus-deficient soil was increased by spraying the leaves daily for 5 weeks with a solution containing nitrogen, phosphorus and potassium.

These experiments established that sprays containing several nutrients could increase the nutrient content of plants by as much as 100 per cent, and might in some circumstances cause similar increases in dry weight. They did not prove, however, that nitrogen, phosphorus and potassium were all absorbed by leaves, because absorp-

tion of one nutrient by the leaves might have increased uptake of others by the roots. In order to distinguish the effects of individual nutrients, sprays supplying nitrogen, phosphorus and potassium separately, and in all combinations, were tested on sugar beet (Thorne, 1955). All three nutrients were absorbed through the leaves, and uptake of any one of them was unaffected by the presence of others in the spray. Spraying with nitrogen-containing sprays increased the absorption of phosphorus and potassium by the roots from the soil, and potassium in sprays increased the uptake of phosphorus from the soil.

Nitrogen, but not phosphorus or potassium, fertilizer added to the soil increased the leaf area of sugar beet, and hence also the quantity of nitrogen retained and absorbed by the leaves from an ammonium nitrate spray (Thorne, 1955). None of the nutrients applied to the soil affected the percentage of the nitrogen retained on the leaf that entered the plant. Rodney (1952) showed that apple leaves absorb nitrogen equally easily from sprays of urea, calcium nitrate or ammonium sulphate, and the same result was found for sugar beet (Thorne, 1954). Urea is absorbed very quickly by the leaves of apple, and probably also other species (Cook and Boynton, 1952; Hinsvark *et al.*, 1953). In 2 hours the lower surface of young apple leaves absorbed 60 per cent of the applied urea and the upper surface 13 per cent; after 24 hours the corresponding figures were 80 and 20 per cent. Urea uptake by the lower surface during 2 hours was increased by high leaf nitrogen, unaffected by reducing the carbohydrate in the leaf by shading, and reduced by adding sucrose to the urea spray.

The amount of phosphorus retained and absorbed by leaves of sugar beet from a sodium phosphate spray was increased by nitrogen fertilizer added to the soil, and the percentage absorbed was also apparently slightly increased by nitrogen fertilizer, but unaffected by phosphorus or potassium (Thorne, 1955). Phosphorus uptake by the roots of swedes grown in a very high phosphorus nutrient solution was reduced when phosphorus was applied to the leaves (p. 66). The uptake of phosphorus from a variety of compounds supplied in sprays has been studied by Silberstein and Wittwer (1951), who found that the growth of tomato, maize and French-beans was increased by ortho-phosphoric acid and potassium and ammonium phosphates, but magnesium phosphate and most organic phosphates had little effect. Autoradiographs of whole plants of tomato, maize and French-bean, made a few hours after applying radio-active phosphorus to the leaves, showed that phosphorus is absorbed and translocated to other parts of the plant very rapidly (Silberstein and Wittwer, 1951; Wittwer and Lundahl, 1951). Absorption of ^{32}P by swede leaves increased for 2–3 days after a single application, and then remained constant for another 10 days at about 50 per cent of the amount applied (p. 67). Trebling the concentration of the solution applied to the leaves increased the percentage absorbed slightly, but significantly.

Potassium uptake by sugar-beet leaves from KCl sprays was increased by nitrogen applied to the soil in the same way as was nitrogen and phosphorus uptake. The percentage of the applied potassium absorbed by the leaves appeared to be slightly increased by nitrogen added to the soil, and reduced by potassium. The

latter effect may be due to reduced uptake by the roots of plants with a high supply of potassium from the soil when sprayed with potassium, because there was no accumulation of unabsorbed potassium on the surface of the leaves (*cf.* phosphorus uptake by swedes).

The quantity of nutrient remaining on the surface of sprayed leaves of sugar beet and removed by washing before harvest was small, showing that most of the nutrient retained by the leaves from sprays was absorbed. Therefore the percentage recoveries of nutrients from sprays were greater than those obtained from fertilizer applied to the soil at sowing (Thorne, 1955). Usually a slightly greater proportion of nutrient applied in sprays than of nutrient applied to the soil remained in the tops. The dry weight increases per unit of nutrient absorbed through the roots were greater than for nutrient absorbed through the leaves. Both these differences between nutrients applied to leaves and soil may be related to the later uptake from sprays; fertilizer nutrients were all applied to the soil at sowing, and those in the spray were supplied continuously throughout the growing season.

The mechanism of leaf absorption is not understood. Nutrients must be able to pass through the cuticle, because urea is absorbed by both surfaces of the hypostomatous apple leaf (Rodney, 1952; Cook and Boynton, 1952). Boynton (1954) claims that absorption also occurs through the stomata, but Fogg (1947) considers this unlikely on theoretical grounds. There is a continuous path of hydrophilic pectic substance from discontinuities in the cutin covering McIntosh apple leaves to the vascular bundle sheaths, along which water-soluble substances could pass (Roberts *et al.*, 1948). Absorption continues, however, long after the leaf is apparently dry, and spraying with water after a phosphate spray had dried did not increase phosphorus uptake by swede leaves (p. 67).

It can be concluded from pot experiments that nitrogen, phosphorus and potassium can all be absorbed by leaves from sprays and that most of the nutrient retained on the leaf is probably absorbed, often within a few days of application. Therefore recoveries in the plant of nutrients applied in sprays are normally greater than of nutrients applied to the soil. In spite of this, the effects on growth of nutrients applied in sprays were smaller than those of nutrients applied to the soil, but this difference would not necessarily occur in pots or in the field if fertilizers were applied simultaneously to soil and leaves.

FIELD EXPERIMENTS

Nutrients supplied in sprays will only be absorbed by the leaves of field crops if the volume of solution applied per acre is sufficiently small for most of it to be retained by the leaves and not fall on the soil. Because of this limitation on the volume of spray solution, the quantity of nutrient that can be applied in a single spraying is restricted by the solubility of the fertilizers and the danger of scorching the leaves. Nitrogen is the best major nutrient for application by this method, because, as both urea and ammonium nitrate are highly soluble and rich in nitrogen, dilute solutions contain a relatively high concentration of nitrogen. Urea usually scorches less than ammonium nitrate.

Nitrogen uptake by sugar-beet plants from six sprays of 3 per cent ammonium nitrate or an equivalent urea solution, applied at 100 gal./acre in September, was twice that obtained from similar solutions applied to the soil between the rows (Report of Rothamsted Experimental Station for 1952, p. 67). Seventy per cent of the nitrogen applied in leaf sprays, whether as ammonium nitrate or urea, was recovered in the plant, and 30 per cent was converted into leaf protein. The distribution in the plant was the same for nitrogen absorbed through leaves or roots. In another experiment nitrogen uptake from four 3·4 per cent urea sprays, applied at 100 gal./acre or from one spray of 54·7 per cent urea applied at 25 gal./acre, did not differ significantly, although there was some scorching by the more concentrated spray (Report of Rothamsted Experimental Station for 1953, p. 70). Spraying winter wheat at ear emergence with 3 per cent NH_4NO_3 at 100 gal./acre increased the yield and nitrogen content of grain and straw to the same extent as applying the same solution to the soil at the same time (Report of Rothamsted Experimental Station for 1953, p. 70). Nitrogen applied as urea sprays also had the same effect as soil dressings of urea or other nitrogenous fertilizers on yield and nitrogen content of grass–clover leys, Italian ryegrass (Low and Armitage, 1954) and cereals when given in spring or ear-emergence application (Jealott's Hill, 1953). Urea solutions ranging in concentration from 11 to 44 per cent were used as sprays and applied at 20 gal./acre. Soil dressings and urea sprays have been shown to be equally effective methods of nitrogen application to tomatoes (Montelaro *et al.*, 1952), maize (Foy *et al.*, 1953) and sugar cane (Hawaiian Sugar Planters' Association, 1951). Urea sprays are frequently applied to apple trees, and give responses equal to, or better than, those obtained from soil dressings (Fisher 1952). Tolhurst and Bould (1952) have shown that nitrogen applied to apple trees as urea sprays does not kill the clover in the cover crop, as do soil dressings, and that trees grown in a non-leguminous sward benefit from urea sprays, whereas all the nitrogen in a soil dressing is utilized by the grass.

Spray application of phosphorus, which is easily fixed in the soil, might be an economical method of using the element, but phosphorus appears to have been applied in sprays much less frequently than nitrogen. This may be because annual agricultural crops require phosphorus early in the season when there is only a small leaf area to retain the spray, and because many phosphorus compounds have a low solubility. Silberstein and Wittwer (1951) report an experiment in which 2·7 lb. P_2O_5 per acre applied in four sprays of ortho-phosphoric or glycero-phosphoric acid increased the early yield of tomatoes more than did 135 lb. P_2O_5 per acre applied to the soil as superphosphate before transplanting. However, the total yield was significantly increased only by the soil dressing. Sugar cane is reported to respond well to 8 lb. P_2O_5 per acre applied as a super-phosphate solution (Hawaiian Sugar Planters' Association, 1951).

Examples of spray application of potassium are also scarce, although the results that have been reported indicate that the method may be useful. The potash content of a crop of lucerne was increased 35 per cent by the application of 65 lb. K_2O per acre in four potassium sulphate sprays, and equivalent soil dressings gave only one-third this increase (Report of Rothamsted Experimental

Station for 1953, p. 70). The potash content of the crop was already high, and neither leaf nor soil application caused any increase in yield. Tropical crops might benefit from potash application in sprays, because many tropical soils are low in potassium and do not respond well to soil dressings. The yield of sugar cane and potassium per cent of dry weight of the sheaths were the same 5 months after receiving 19 lb. K_2O per acre as a spray as after 200 lb. K_2O applied to the soil (Hawaiian Sugar Planters' Association, 1951). The potassium spray was a 28·5 per cent solution of muriate of potash applied from the air at 10 gal./acre.

Nutrients can be applied in sprays with each other, with pesticides, herbicides, etc., or with trace elements. Several commercial highly soluble mixed fertilizers have been developed for application in solution to leaves or soil, and some have been used experimentally (Gillern, 1950; Arvan and Mowry, 1954; Pirone, 1952). The concentration of salts in a mixed nutrient spray is limited by their solubility and the danger of scorching, so that several applications are required to supply the same quantity of one nutrient as can be applied alone in a single spraying or as a soil dressing. When nutrients are added to fungicidal or insecticidal sprays the phytotoxicity may be increased. According to Hamilton *et al.* (1943), lime added to the spray reduced the injury to apple foliage caused by spraying with sodium or potassium nitrate or ammonium sulphate mixed with wettable sulphur and lead arsenate. Urea caused less damage than other forms of nitrogen when mixed with insecticides. Vegetable crops were damaged by sprays containing ammonium nitrate and arsenicals unless lime was also added, but urea was safe with a number of insecticides and fungicides (Isaacs and Hester, 1954). It is suggested that ammonium nitrate increases and lime decreases the solubility of the arsenates. A 51 per cent solution of ammonium nitrate or a 40 per cent solution of urea was safely applied to winter wheat in April, either alone or mixed with 2-4D (p. 67). Micro-nutrients can be mixed with major nutrients in sprays or applied alone, and the small quantities required can be easily supplied in a single dilute spray. Trace-element deficiencies are frequently due to soil conditions making the element unavailable to the plant, and are therefore often cured more easily by sprays than by soil application, e.g., manganese deficiency in peas and beetroot (Lewis, 1939; Wallace and Ogilvie, 1941) and boron deficiency in turnips (Mac-Lachlan, 1944).

In field experiments the effects of nutrient sprays are usually of the same order as for soil dressings, and rarely more than two or three times greater. Therefore, spray application does not result in a great saving of fertilizer, but may be preferable to soil application when : (1) soil conditions or a competitive crop make nutrients from soil dressings unavailable; (2) an accurately timed response to fertilizer is required, e.g., a change in the composition of a crop late in the season; (3) routine applications of insecticidal or herbicidal sprays, to which nutrients can be added, are made; (4) the growth of the crop prevents application of fertilizer to the soil but permits it to the leaves from a high-clearance sprayer or helicopter. If crops are to absorb nutrients applied in sprays through their leaves there must be sufficient leaf surface to retain the spray. This limits the usefulness of the application of nutrients in sprays to annual

agricultural crops, because those most in need of fertilizer, i.e., young or starved crops, have only a small leaf area. Application of sprays is liable to be more expensive than traditional methods of fertilizer distribution, and therefore not economically justifiable, even when a saving in fertilizer results. Thus, although it is now well established that fertilizers applied in leaf sprays can be absorbed by crops and in some circumstances are more effective than fertilizers applied to the soil, the method is not likely to become very widespread. Apart from these practical considerations, nutrient absorption through leaves may prove very useful in theoretical studies on plant nutrition.

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