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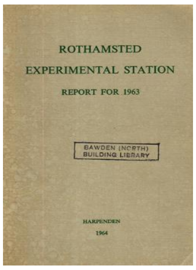

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MOBILISATION PHENOMENA IN SOILS

C. BLOOMFIELD

The translocation of iron is a dominant feature in the development of several important soil groups; our work has been mainly devoted to the study of the mobilisation of iron in the soil, particularly in relation to the processes of gley and podzol formation.

Mobilisation under non-sterile conditions

Reducing conditions develop when a soil is waterlogged; iron is mobilised in the ferrous form and the red to brown colour of ferric oxide is eventually replaced by a neutral grey colour. This process can be studied in the laboratory by adding plant material, e.g., dried grass, to a flooded soil and incubating the mixture anaerobically in the dark. Considerable amounts of soluble ferrous compounds are formed in a few days, and further quantities can be extracted from the soil by successive leaching with neutral and acid (pH 3) ammonium acetate solutions. All three extracts give positive reactions for ferrous iron with reagents such as 2,2′-dipyridyl, and ferric oxide is precipitated from the water and neutral acetate extracts when they are aerated. It can thus be assumed that these fractions represent ferrous iron formed during incubation, but as will be shown later, it is not certain to what extent the reduced state of iron extracted at pH 3 is an artefact of the acid extraction process.

Aerated water extracts of incubated soils retain considerable amounts of iron in solution, even at pH values greater than 7, so that the presence of complex compounds is indicated (Bloomfield, 1951).

Colorimetric determination of ferrous iron in fermentation reaction solutions invariably gives values considerably less than the total iron determined after destruction of organic matter. Hutchinson (1957) quotes similar observations on lake waters. Grass fermentation solutions prepared in the presence of ferric oxide reduce ferric iron when the reaction solution is treated with a solution of a ferric salt. This residual reducing capacity is considerable, being several times greater than the amount of ferric oxide dissolved during incubation, and it seems reasonable to assume that the difference between the total and apparent ferrous iron in the reaction solution represents ferrous iron in complex form.

That complexes of stability comparable with that of ferrous 2,2′-dipyridyl may be formed in these experiments was demonstrated by treating a water extract of anaerobically fermented grass with known amounts of ferrous sulphate. Theoretical recoveries were obtained when dipyridyl-reactive ferrous iron was determined immediately after adding the ferrous sulphate, but recoveries were low when the mixture was left for 24 hours before adding dipyridyl. When left for 24 hours after adding the reagent the apparent ferrous contents approached the theoretical values; the achievement of equilibrium in these systems is thus relatively slow.

These results show that misleading values are obtained when iron is determined directly in solutions such as these without first destroying organic matter. For this reason we have taken the total iron content of a reaction solution as the only reliable measure of mobilisation. Organic matter extracted from soils behaves in the same manner—for example, in his method for determining "free ferric oxide" in soils, Mackenzie (1954) relies on boiling with hydrogen peroxide to destroy organic matter extracted by dithionite solution. With a normally humose topsoil we find this procedure gave values some 15% smaller than those obtained after evaporating the extract with nitric acid. The discrepancy was considerably smaller with the less humose subsoil.

Up to a certain value the amount of iron mobilised is increased by increasing the proportion of plant material in the reaction mixture. Beyond this point further increase in the organic content has little effect on total mobilisation, but the water and neutral acetate fractions increase, largely at the expense of the acid acetate fraction.

Sulphate is reduced to sulphide under conditions such as those described above. Presumably some sulphate is always present in systems containing plant material, so that to this extent sulphate reduction will always be involved in natural gley formation—it is possible that in grass fermentation experiments the iron retained at pH 7, but extracted at pH 3, represents ferrous sulphide thus formed. However, sulphide is not detectable in many natural gley soils, and sulphidic and non-sulphidic gley soils are readily distinguishable in the field. Starkey and Halvorson (1927), Allison and Scarseth (1942), Bloomfield (1950) and Bétrémieux (1951), observed very extensive solution-reducation of ferric compounds when soil is incubated anaerobically with glucose; neutral grey residues resembling naturally gleyed soil are produced. Under these conditions sulphate is virtually absent, and we regard this process as non-sulphidic gleying. In the subsequent discussion "gleying" or "gley" refer to this type of process or its product; sulphate reduction is regarded as a secondary process, and is referred to as such.

In our experience reagents such as ammonium acetate, acetyl acetone, etc., extract only barely detectable traces of iron from naturally occurring gley soils; this suggests that, under the conditions in which these soils are formed, mobilised iron is either lost from the profile or reprecipitated to form the ferric oxide stains and concretions that are characteristic of periodically waterlogged soils.

From the foregoing it seems that the grey colour of a gley soil results from the removal of superficial coatings of ferric oxide, but whether formed naturally or prepared in the laboratory, the residual material retains a large proportion of its original iron content. Considerable amounts of iron can be removed from gley soils by any of the methods used to determine "free ferric oxide", so that not all of the residual iron is included in unweathered minerals.

The absence of the characteristic red, yellow or brown colours of ferric oxides in soils containing 4–5% total iron suggests that the iron is present

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in the ferrous state, but as the grey colour does not change on exposure to the atmosphere, it becomes necessary to postulate that the iron is combined in such a way as to be stable to atmospheric oxidation.

Determination of ferrous iron in soils. It might be thought that it would be a simple matter to determine ferrous iron in a soil, but unfortunately this is not so. Various methods have been proposed, but in our experience none of these is reliable. These methods fall into two groups; either extractants such as dilute sulphuric acid (Ponnamperuma, 1955), or aqueous aluminium chloride solutions are used to extract ferrous iron, or ferrous iron is liberated by dissolving the soil in hydrofluoric acid. Ferrous iron included in silicate minerals is of little interest in this connection, and the use of hydrofluoric acid suffers from the defect that iron from this source is included in the final result. However, both methods suffer from the much more serious objection that ferric iron is readily reduced by organic matter when a soil is treated with mineral acid. This effect has been demonstrated by adding increasing amounts of ferric oxide to an ungleyed humose soil before determining the apparent ferrous iron by the hydrofluoric acid method of Walker and Sherman (1962). The apparent ferrous content increased with increasing additional ferric oxide to a value that presumably corresponded to the reducing capacity of the soil organic matter, and thereafter remained constant. The untreated soil gave identical ferrous and total iron contents, but on this evidence it cannot be assumed that the soil contained any ferrous iron at all (Bloomfield, unpublished).

Similar but less extensive interference by organic matter is experienced when soils are extracted with dilute acids. This effect was observed by Morison and Doyne (1914), but their work does not appear to have received the attention it deserves.

Ignatieff (1937) introduced the use of dilute aluminium chloride solution for the extraction of ferrous iron from soils. It is difficult to see why Ignatieff's reagent should differ in this respect from hydrochloric acid of equivalent acidity, although we find it causes less reduction than the mineral acid solutions used by Ponnamperuma and others. However, although the error is small its magnitude is comparable with ferrous contents that have been reported, for example, by Daniels and collaborators (1961). From the description of the soils used in this investigation it is certain that some, but not all, contained ferrous sulphide; these soils gave comparatively large values for extractable iron. Ferrous sulphide is dissolved by Ignatieff's reagent, but not sufficiently rapidly to ensure complete solution in a reasonable time, and reduction of ferric iron by the liberated hydrogen sulphide causes further complication. No doubt the same criticisms apply to the extractants proposed by Kumada and Asami (1958) and Takai and collaborators (1958), i.e., *n*-sodium acetate of pH 2·8 and 3·0 respectively.

As measured by the evolution of hydrogen sulphide, we find that extraction for 30 minutes in an inert atmosphere with molar ammonium acetate at pH 4·5 causes little attack on ferrous sulphide. This reagent gives a reasonable compromise between the competing requirements of avoiding such attack and ensuring complete extraction of non-sulphide ferrous iron from laboratory preparations, but with field samples in which the total amount of extractable iron is small, the error would still be appreciable.

The colour of gley soils. If values obviously relating to ferrous sulphide-containing soils are excluded, it is apparent that the amount of extractable ferrous iron in gley soils is very small. Nevertheless, when lumps of wet gley soil are kept moist under conditions allowing surface oxidation to occur, i.e., by storing in a thin polythene bag, deposits of ferric oxide often form at air–water and air–soil interfaces. It seems therefore that small amounts of ferrous compounds occur in the soil solution, but that re-oxidation is visible only when diffusion within the soil mass causes concentration at areas of selective oxidation. Paradoxically, this effect is greatest with soils containing sulphide—see below. Ferrous iron is sorbed from solution on hydrous ferric oxides, and in this state is readily oxidised. Ferric oxide may thus act as a catalyst in promoting the formation of ferruginous deposits (Bloomfield, 1951).

The grey colour of gley soils thus cannot be ascribed to the presence of readily extractable ferrous compounds, and, apart from primary minerals, residual iron in gley soils must either be present as insoluble secondary ferrous compounds, in which case its stability to reoxidation poses a problem, or as ferric oxide which for some reason does not impart its characteristic colour to the soil. The small amount of iron that can be extracted from non-sulphide gley soils with reagents such as acid ammonium acetate, and the unchanged colour of the extracted soil, suggest that the grey colour is unlikely to be due to the presence of ferrous compounds, and some measure of support for this view was obtained by determining the total iron and apparent ferrous contents of a pale-grey sulphide-free soil after dissolution in hydrofluoric acid. The organic carbon content of the soil was 1%, so that it is certain that the apparent ferrous value would be excessively high, but even so, on the face value of the results as much as 40% of the total iron was in the ferric form. Although the state of the residual iron in a gleyed soil thus remains uncertain, the balance of evidence seems to suggest that apart from ferrous iron in primary minerals, the residual iron is most likely to be in the ferric form.

Confusion over this question is involved in a recent discussion of the nature of gumbotil—the name given by American workers to a heavy clay material formed by the weathering of glacial till. Kay and Pierce (1920) concluded that the persistence of grey colours under aerobic conditions proves the absence of ferrous iron. Leighton and MacClintock (1962) quote analyses showing that the ratio of ferrous to ferric oxide is greater in the unweathered till than in the surface gumbotil, and from this they conclude that the formation of gumbotil is an oxidative process; they disagree with the view ". . . of some pedologists and geologists (that) the grey colour is due to biologic reduction of ferric iron". Our results lead us to conclude that gleying causes the solution and reduction of superficial ferric oxide coatings, and that the mobilised iron either drains or diffuses from the system, or is reoxidised and precipitated on contact with air, along root channels for example (Bloomfield, 1952). If insoluble ferrous sulphide were formed, this, too, would be readily reoxidised. So far as they are not a measure of the organic content therefore, the ferrous iron values given by Leighton and MacClintock probably merely reflect the presence of unweathered minerals, and can give no indication of the mode of formation of the soil. The fact remains that reduction, either chemical or microbiological, is the only process shown experimentally to be capable of producing material such as gumbotil or gley soils.

Mobilisation of trace elements in flooded soils. Oxides of several trace elements are dissolved by the action of anaerobically fermenting plant material and, as with iron, sterile aqueous extracts of undecomposed plant material are in general rather less effective. The dissolved metals are in true solution and in complex form. Manganese, copper, chromium, cobalt, nickel, zinc, lead, vanadium (and also phosphate) are mobilised when soils are incubated anaerobically with plant matter. Molybdenum is also mobilised under these conditions, as would be expected from the fact that teart is most commonly found on poorly drained soils. The availability of soil molybdenum is normally increased by raising the pH of the soil, but mobilisation of molybdenum has been observed in these experiments in conditions of increasing acidity; solution of molybdenum under these conditions is therefore something other than a simple pH effect, and may involve the formation of organic compounds. However, it may be that under these conditions mobilisation of molybdenum is the result of organic matter preventing sorption of molybdate on ferric oxides, rather than a specific molybdenum–organic interaction.

Copper, and to a smaller extent nickel, are strongly sorbed by unhumified plant fibre; nickel thus sorbed during anaerobic incubation appears to be desorbed when the system is aerated. Copper is readily mobilised by sterile water extracts of grass.

Aeration of anaerobically mobilised trace elements does not cause them to be precipitated unless ferrous iron is present, when significant amounts are usually coprecipitated with ferric oxide. Much iron is immobilised when incubated soils are aerated, and although drying further decreases the extractability of iron, in general the net result of flooding and air-drying is to increase the extractability of all the elements we have studied (Gasser and Bloomfield, 1955; Ng and Bloomfield, 1961, 1962).

Preliminary results show that appreciable amounts of iron, manganese, copper, nickel, cobalt and molybdenum are mobilised when moist soils are incubated aerobically with plant material.

Sulphate reduction. Microbial reduction of sulphate in soil causes the formation of ferrous sulphide, and the process is not uncommon in gley soils. Although the process has been extensively studied in connection with rice soils and with the corrosion of buried steel pipes, pedologists seem not to have considered sulphate reduction in its true perspective in relation to gley soils. Byers and collaborators (1938) distinguish between grey soils formed under conditions of impeded drainage, and "bluish or greenish waterlogged horizons sometimes called gley". From the context, the latter appear to be soils containing sulphide, and these are referred to as "true gley". Soils containing ferrous sulphide usually turn brown on exposure to

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the air; it is therefore implicit in the description of gley soils given in the *Soil Survey Manual of the U.S. Department of Agriculture* (1951) that true gley soils are sulphidic.

Robinson (1949), without qualification, ascribed the colour of gley soils to the presence of ferrous sulphide or phosphate. Ferrous phosphate seems to occur comparatively rarely, and to have been conclusively demonstrated only in the form of minute discrete particles. Many natural gley soils contain no detectable sulphide, and indeed the total sulphur and phosphorus present is usually equivalent to only a very small fraction of the total iron content.

Failure to distinguish between sulphide-containing and sulphide-free gley soils can only lead to confusion. For example, Ignatieff (1937, 1940) and Walker and Sherman (1962) seem to make no distinction between the two types in their work on the determination of ferrous iron in soils, and Daniels and co-workers (1961) apparently include both types of soil in their attempt to correlate the colours of gley soils with ferrous iron content. Motomura (1962) apparently did not consider the effects of the sulphate reduction process in his investigation of the effect of nitrogen compounds, e.g., ammonium sulphate, on the mobilisation of iron. In a study of warpland soils in Yorkshire, Heathcote (1951) records the distribution of "free ferric oxide", but as it is apparent from the description of the soils that some contained sulphide, ferrous sulphide has been returned as "free ferric oxide", thereby giving the anomolous result that ferric oxides are apparently concentrated in strongly gleyed horizons.

Although it seems to be true that only soils containing sulphide turn brown on exposure, not all sulphidic soils behave in this way; whether or not reoxidation causes visible browning seems to depend on the content of organic matter, as well as on the sulphide content.

When soils containing ferrous sulphide are aerated they often become very acid and the characteristics of sulphide and non-sulphide containing soils are so different that the most important single division must surely be based on the presence or absence of sulphide.

Sulphate reduction takes place only under strongly reducing conditions, so that gleying probably precedes sulphate reduction. To this extent sulphate reduction might be considered as a secondary process superimposed on gleying proper; in our experience, when sulphate reduction is involved this dominates the process, and it is regrettable that investigations of the chemistry of waterlogged soils, in which the presence or absence of sulphide is an unconsidered variable, should continue to be reported.

Sulphate disappears rapidly after flooding in laboratory experiments, and although soluble ferrous compounds and excess ferric oxide are present, as much as half the sulphur present may be lost from the system as hydrogen sulphide. The proportion of sulphur lost in this way is very strongly affected by comparatively small changes in the pH of the system—a slight increase in acidity causes a relatively large decrease in the amount of ferrous sulphide formed. It has been observed in Japan and elsewhere that the roots of rice plants grown in soils containing little iron are often damaged by hydrogen sulphide. This has been ascribed to the presence of insufficient iron to immobilise the sulphide, but this may not be the true explanation, as we find that relatively large amounts of hydrogen sulphide can be lost in the presence of excess iron; it may be that release of hydrogen sulphide results from too great an acidity rather than from a deficiency of iron.

Motomura (1962) observed enhanced mobilisation of iron in soils incubated with ammonium sulphate, and he concluded that the presence of ammonium salts increases microbiological activity, and hence the formation of ferrous iron. In view of the relatively small nitrogen requirements of micro-organisms, nitrogen seems unlikely to be a limiting factor in systems such as these, and as we have observed enhanced solution-reduction of iron in the presence of sodium sulphate, the effect appears to be specifically associated with sulphate reduction.

If ferrous sulphide were formed by reaction between hydrogen sulphide and ferric oxide, it would be expected that elemental sulphur would be formed according to the equation:

$$Fe_2O_3 + 3H_2S = 2FeS + 3H_2O + S$$

We have found no evidence to indicate that this reaction takes place in laboratory incubations; within experimental error the sum of the residual sulphate and the sulphate equivalents of the ferrous and hydrogen sulphides accounts for all the sulphate originally present. Using thermodynamics, Berner (1963) deduced that polysulphides would be formed in marine sediments under conditions similar to those of our experiments; the complete recovery of sulphur by our analytical methods suggests that little if any pyrite is formed, which is perhaps not surprising in such short periods. Our results could be explained if ferrous sulphide were formed only by reaction between hydrogen sulphide and ferrous iron, but it is difficult to believe that ferric oxides would not be directly involved to some extent.

Mobilisation under Sterile Conditions

The extent of anaerobic solution of ferric oxide by sterile water extracts of grasses is much smaller than that produced by tree-leaf extracts. The greater activity of tree leaves is correlated with the presence of polyphenols, and our results indicate that these are the most important single group of compounds involved in the aseptic mobilisation of iron by leaf extracts (Bloomfield 1957). Schnitzer and DeLong (1955a, b) consider that acidic polysaccharides are the active agents, but we could not detect any mobilisation of iron by purified polysaccharides extracted from aspen leaves (Bloomfield, 1958), and MacLean and DeLong (1956) found no correlation between content of polysaccharides and iron mobilisation.

Sterile water extracts of the leaves, and the barks of some of the 30 or so species tested, dissolve considerable amounts of ferric oxide, even at artificially high pH values (7–8) and under aerobic conditions, although the extent of solution is decreased by aeration or by raising the pH of the system.

After contact with ferric oxide under anaerobic conditions, in the dark, leaf extracts give positive tests for ferrous iron with 2,2′-dipyridyl, and although in the presence of organic matter this is not proof that the iron existed in the ferrous state before addition of the reagent, in conjunction with the fact that the net extent of solution is lower in the presence of oxygen, it seems reasonable to assume that ferric iron is reduced in the process of mobilisation. As in fermentation experiments, the total dissolved iron exceeds the amount determined by dipyridyl, although the residual reducing capacity of the reaction solution is considerable. Aqueous extracts of Scots pine needles have the same effect on the recovery of ferrous iron as that described above for fermented grass extracts, so that here again the formation of complexes of considerable stability is indicated (Bloomfield, 1953).

Reaction solutions are usually dark blue-black; although the coloured compounds are retained, considerable quantities of iron pass through the membrane when a leaf extract–ferric oxide reaction solution is dialysed through Cellophane. Dialysates react with 2,2′-dipyridyl, and on exposure to atmospheric oxidation they slowly develop the blue colour of the original reaction solution. This suggests that oxidation of organic compounds by ferric iron is involved in the production of the colour of the original solution; the behaviour on dialysis indicates that colloidal properties may develop at the same stage (Bloomfield, 1958).

When expressed as the amount of iron dissolved per unit weight of original leaf material, the net solution of iron is decreased by increasing the concentration of the extract. This non-stoichiometric behaviour apparently arises because reaction products are sorbed on residual ferric oxide; this was demonstrated by passing reaction solutions through columns of ferric oxide-coated quartz sand, when iron was retained in the column and could not be removed by washing with water. The sorbed material inhibits further solution of the oxide, presumably by interposing a barrier between the extract and unreacted ferric oxide (Bloomfield, 1955b).

This behaviour suggests a possible connection with the deposition of iron and organic matter in the illuvial horizon of a podzol and, indeed, reasonably close reproductions of podzolised profiles have been made in the laboratory by treating columns of ferruginous sand with dilute leaf extracts (Bloomfield, 1955a, 1956b).

Polyphenols are almost completely removed when leaf extracts are passed slowly through ferric oxide columns, and although under static conditions the extracts will dissolve comparatively large amounts of ferric oxide, the net removal of iron from the column is very small. For example, after slow passage through a column of kieselguhr-supported ferric oxide, 98% of the polyphenols were removed from an oak-leaf extract, and the effluent contained iron equivalent to only 0·5 mg % of the original oven-dry leaf material. Under static conditions the corresponding iron figure would be about 200 mg/100 g of dry leaf. In these experiments the pH values of the effluents usually lie between 7 and 8, compared with values of 4·5–5·0 for the original extracts. Water-extractable polyphenols in leaves falling during autumn have a wide range of molecular weights, and those with larger molecular weights include quite strongly acidic compounds; presumably the retention of these compounds in the column is responsible for the increased alkalinity of the effluents.

Preliminary results indicate that some nitrogen compounds are retained in the columns, but this needs confirmation, as the maintenance of sterility is difficult over the long periods required by these experiments.

Comparatively few species are normally considered as podzol formers, yet all the species tested give leaf extracts that mobilise iron to a greater or lesser extent; in general, broad-leaved species are more reactive than conifers, although podzolisation is most often associated with the latter. It follows that unless a completely different mechanism is in fact responsible for podzolisation, factors that counteract the mobilising action of material leached from the litter must operate in unpodzolised wooded areas.

Kubiena (1953) considers that iron podzols develop under acid-tolerant oak woods in Northern Europe, and Scheys and collaborators (1954) describe podzols under deciduous cover. By means of pollen analysis Dimbleby and Gill (1955) established that podzols formed under beech in the New Forest, and they consider that this applies to base-poor areas throughout Britain. Avery (1958) described micro-podzols formed under beech in the Chiltern Hills, and Mackney (1961) demonstrated by pollen analysis that podzols at Sutton Park in Warwickshire formed under the influence of the present oak cover. Ashley (priv. comm.) reported a podzol in Northumberland which, from the history of the site, has developed after 30–40 years under Japanese larch. There is thus ample evidence that podzols can be formed by species other than those normally considered as podzol formers.

The palatability of tree litter to soil fauna differs from species to species, and it is reasonable to suppose that there are also differences in the rates of enzymic oxidation of polyphenols in fallen leaves. These factors probably contribute in determining the podzolising effect of a particular species under given climatic and other conditions.

Enzymic oxidation of polyphenols in fallen leaves decreases the activity of their water extracts, but in some instances our results indicate that the activity may first rise to a maximum before it finally decreases to a quite small value. This appears to be the reason for freshly fallen larch needles being more active than those picked from the tree a few weeks before leaf fall (Bloomfield, 1954a).

Lossaint (1959) found that the activities of extracts of aged leaves of alder, hornbeam and two oak species, decrease less than those of beech, spruce, fir and pine. It is significant that the species least affected by ageing are those more commonly associated with podzolisation.

Schnitzer and DeLong (1955a, b), and Lossaint, consider that the mobilisation of iron by soluble leaf constituents is essentially a process of colloidal peptisation, a view difficult to reconcile with the evidence they adduce for the formation of ferrous compounds. Unless an initial solution stage intervenes, it is necessary to postulate, as apparently do Yarkov (1954), Mandal (1961) and others, that a solid phase reduction of ferric oxide is possible under ordinary soil conditions. Schnitzer and DeLong, and Lossaint, apparently worked exclusively with aerobic systems, and they were therefore probably dealing with the products of reoxidation; this interpretation of their results is favoured by the fact that Schnitzer found that the ferric to ferrous ratio of mobilised iron was increased by shaking the reaction mixture, presumably in the presence of air (Bloomfield, 1958).

This illustrates the danger involved in making laboratory models for soil processes, and the advantages of studying simplified systems, as, for example, by excluding the possibility of atmospheric reoxidation in the experiments discussed above. Similarly, it may be noted that Lossaint used soil columns in assessing the relative activities of various tree species. Under these conditions the results would relate only to the net excess of solution over sorption, under conditions permitting the latter to be fully expressed, and which certainly increase the difficulty of detecting the operation of competing reactions.

Hingston (1963) notes that because of the competing influences of solution of iron compounds and precipitation of iron–polyphenol complexes, there is no simple correlation between total polyphenol content and the amount of iron mobilised under aerobic conditions. It might be added that under anaerobic conditions resorption phenomena similarly obscure any such correlation.

Lossaint attempted to measure the total reducing capacities of leaf extracts by adding ferric ammonium sulphate and determining the excess ferric iron. Apart from the uncertainty caused by complex formation, we find this procedure unsatisfactory because of the formation of flocculent precipitates when leaf extracts are treated with electrolytes. Probably because of this and associated sorption effects, Lossaint found the specific reducing capacity of an extract to vary with its concentration in the same way we find the specific capacity of an extract to dissolve ferric oxide to increase with dilution. The decrease of reducing capacity with increasing pH that Lossaint observed might have resulted from atmospheric oxidation of polyphenols, a process favoured by increased alkalinity.

It has been realised for a long time that nutrients are leached from growing leaves by rainwater (Dalbro, 1955). Schnitzer and DeLong (1954) showed that material able to dissolve and reduce ferric oxide is present in water dripping from the growing canopy, and Davies and collaborators (1960) confirmed this observation. As they found little activity in extracts of surface litter, Davies considers this to be the most effective mechanism by which iron-mobilising plant constituents enter the soil, and suggests that the activity we observe is derived from material leached from the canopy into the surface litter (Coulson *et al.*, 1960). However, any such tendency could not have operated, as in all our work on deciduous species we have used freshly fallen autumn leaves which were collected daily. Paper chromatography of water-soluble polyphenols of autumn-fallen leaves that were dried under forced draught at 105° C immediately after collection, shows that compounds of large molecular weights constitute by far the greater part of the total phenolic material, and on quantitative grounds must account for most of the activity of the extracts. (This apparently drastic drying treatment is necessary to inactivate enzymes; rapid drying under these conditions appears to cause much less change than slower drying at a lower temperature. Coulson and his co-workers found polyphenols were lost from leaves dried for 3 days at 25° C before being ground and stored.) The amount of oak-leaf polyphenols extracted by 50%

methanol decreases when the leaves are exposed in the field in such a way as to prevent attack by soil fauna; after three months' exposure large molecular weight constituents are no longer extracted, and only a very small amount of one compound giving a discrete spot on the chromatogram remains. Presumably polyphenols extractable by water would decrease even more rapidly. Coulson and his co-workers may have used litter that had lost its activity in this way. With picked leaves they found most of the phenolic constituents to be small enough to move as discrete spots on paper chromatograms; this probably resulted from their practice of freezing leaves in liquid air immediately after picking, thus preventing oxidation of simple phenolic compounds. As oxidation of polyphenols presumably occurs to some extent during senescence, autumn-fallen leaves are presumably more relevant to soil processes than leaves picked during growth.

In our investigations of the properties of leaf extracts we have confined ourselves to sterile systems, and it remains to be seen how far microbial action modifies the process. Despite the artificial conditions of our experiments, the laboratory model agrees quite closely with field observations, so that it may be that there are little more than quantitative differences between sterile and non-sterile systems.

We have not investigated the effect of leaf extracts on the mobilisation of trace elements, but Titlyanova and co-workers (1959) found such extracts to be quite effective in desorbing radioactive isotopes of iron, zinc, cobalt and yttrium from soils, but less effective than 0·01 n EDTA. Leaf extracts were more effective than EDTA in desorbing strontium, but none of the extracts removed caesium. The formation of complexes between zinc and the various leaf extracts was demonstrated by the use of exchange resins.

Translocation of Clay

A distinction must be made between the true podzol, in which iron compounds are translocated as such, and sols lessivés, in which ferric oxide apparently moves as a coating on clay particles. In a sol lessivé, although the distribution of iron down the profile resembles that of a podzol, no such differentiation is apparent when the iron content is expressed as a percentage of the clay fraction.

Barshad (1955) reviewed the process of clay movement in soils, and listed the factors tending to promote the displacement of clay. These are negative, in the sense that they represent the absence of flocculating influences, but it seems that active dispersion may be provided by soluble plant constituents, as flocculated clay suspensions are dispersed by very dilute leaf extracts (Bloomfield, 1954b, 1956a). With most plant species kaolinite is reflocculated as the concentration of the extract is increased, but the clay redisperses when it is washed with water, and remains dispersed despite repeated washing. Deflocculation is associated with irreversible sorption of polyphenols; polysaccharides are also involved, but it is not known whether these compounds are sorbed as strongly as are polyphenols.

Washed, treated kaolinite does not flocculate above about pH 4, whereas the original clay flocculates at about pH 9. It is thus possible that, in the presence of plant constituents, clay may be transported under conditions that would normally preclude such movement.

Soil polysaccharides have received much attention in connection with the stabilisation of soil structure, and in our experiments too their action is probably one of stabilisation; the action of polyphenols seems to be one of dispersion.

The Role of Organic Matter in Soil Transformations

Many explanations of soil-forming processes of the type considered above postulate that humic matter (or certain fractions isolated from it, i.e., fulvic, crenic, apocrenic acids, etc.) is the causal agent. We have been unable to detect any mobilising action by humified material, by which we understand the amorphous, dark-coloured colloidal product of the decomposition of plant material, and our results suggest that humus, thus defined, is active as an agent of soil dynamics only in so far as it can act as a source of energy for continued microbial action. This is not to say that humic material does not have important specific properties—for example, its ion exchange and sequestrating properties are important in determining the properties of a soil, and no doubt these properties play an important, but secondary, role in soil development.

It is implicit in many studies of podzols that organic fractions extracted from the B horizon are the agents responsible for the translocation of iron, etc., into this horizon. This could be so only if the processes of mobilisation and immobilisation were purely physical, or of a very simple chemical nature, e.g., the neutralisation of an acid. Our results indicate that reduction of ferric iron is involved in the mobilisation of ferric oxide, so that even if further chemical and microbiological action were not involved, the organic matter of a podzol B horizon is an oxidised and probably polymerised end product of the sequence, and not the causative agent.

Podzols so commonly possess well-developed layers of acid mor humus that the presence of such horizons has come to be regarded as a criterion of the podzol, and the process of podzolisation is often ascribed to the presence of a mor humus layer. Our results suggest that there is no fundamental reason why there should be any connection between podzolisation and the formation of mor, and the fact that the two are so often associated may merely mean that the conditions that favour the development of one also favour the development of the other. It is quite likely, however, that by its action in holding moisture and sealing off the lower horizons, a mor A_0 horizon may favour the development of podzolisation.

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[This paper is so cited for convenience. The correct authorship is "DeLong and Schnitzer".]

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