EFFECT OF MICROORGANISMS ON THE TRANSFORMATION OF MINERAL FRACTIONS IN SOIL

E. G. MULDER AND W. L. VAN VEEN
Laboratory of Microbiology, Agricultural University, Wageningen, The Netherlands

I. INTRODUCTION

Transformation of mineral fractions of the soil is common to higher plants and microorganisms utilizing the inorganic compounds for building up their cellular material. With higher plants this is the case with practically every nutrient including nitrogen. Microorganisms, however, often take up part of their nutrients in the organic form.

The amounts of inorganic compounds involved in this type of transformation, depend on the requirement of the living organisms, i.e. on the amount of cell material synthesized.

Certain types of inorganic salts, upon their absorption by living plants or microorganisms, are submitted to a fargoing transformation (e.g. nitrates and sulphates). Other compounds, however, are only moderately or slightly modified (e.g. phosphates, several trace elements).

In addition to serving assimilatory purposes, mineral matter may serve as the energy supply of certain types of bacteria. This may be achieved by (a) the inorganic compound being the substrate supplying the organism with energy (autotrophic bacteria oxidizing H_2S to S or H_2SO_4, H_2 to H_2O, NH_3 to nitrite and subsequently nitrate etc.).

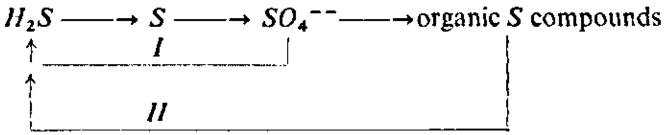
In a different type of microorganism mineral compounds (sulphate, nitrate) are used as the H acceptor. An oxidizable compound, either organic or inorganic, serves as the energy-supplying substrate (sulphate-reducing and denitrifying bacteria).

Microorganisms using the mineral fraction as energy supply or as H acceptor require considerably larger amounts of the inorganic compound than those using it for the synthesis of cell matter. A second difference is concerned with the different type of reaction product formed, viz. organic cell constituents in the latter case as contrasted with inorganic oxidation or reduction products in the former. In both cases the microorganisms by way of enzymatic reactions exert a direct effect on the transformation of the mineral fraction.

In addition to a direct effect, certain types of microorganisms may exert an indirect effect on the transformation of the mineral fraction. This depends on the chemical activity of products formed by the organisms, particularly inorganic and organic acids.

II. TRANSFORMATION OF SULPHUR COMPOUNDS BY MICROBIAL ACTIVITIES

Sulphur, like nitrogen, may occur in various inorganic and organic compounds. This diversity depends on the various states of oxidation of S (from −2 in sulphide to +6 in sulphate). Similar to the transformation of nitrogen, many reactions of sulphur in nature are brought about by microorganisms. The major transformations (*S* cycle) are shown in the following scheme:



The inner cycle (I) represents the important geomicrobial transformations as they are found particularly in certain aquatic environments with external H_2S or sulphate supply (Silverman and Ehrlich, 1964). The reactions of cycle I are involved in the energy metabolism of the participating microorganisms. Cycle II in addition includes the synthesis of organic *S* compounds. The sequence of reactions of cycle II is more representative for soil conditions where synthesis and breakdown of organic S compounds are very important reactions of the cycle.

(a) *Oxidation of H_2S*

The oxidation of H_2S, the most reduced *S* compound in nature, to *S* and subsequently possibly to SO_4^{--} is carried out by three different types of microorganisms viz. ***Beggiatoa***, ***Thiobacillus***, and photoautotrophic bacteria of the Rhodobacteriineae. The former two types derive both energy and reducing power (supply of hydrogen) required for the assimilation of CO_2 from the oxidation reaction, the Thiorhodaceae (purple and green sulphur bacteria) obtain the energy from photoautotrophic reactions while the reduced sulphur compounds are used as the hydrogen donor.

When excessive amounts of H_2S are present, this compound is used as the main substrate by the above-mentioned bacteria while sulphur is stored as intra- or extracellular reserve material. In this way large amounts of biogenic sulphur deposits may be formed in lakes or ponds (Silverman and Ehrlich 1964). When the H_2S supply decreases, the bacteria may transform the stored *S* into SO_4^{--}.

Of the three types of sulphide-oxidizing bacteria only one type (*Thiobacillus*) may occur in soil. Organisms of this genus oxidize sulphide, sulphur, thiosulphate, tetrathionate, and sulphite to sulphate (Starkey 1966). Some species (*T. thiooxidans*, *T. ferrooxidans*) are tolerant to extreme acidity.

In addition to these autotrophic bacteria, several heterotrophs are able to carry out incomplete oxidations of *S* compounds.

(b) *Sulphate reduction*

Sulphate-reducing bacteria are strictly anaerobic organisms which use a variety of organic acids and simple primary alcohols as hydrogen donors and sulphate as hydrogen acceptor; the latter is reduced to H_2S. These bacteria become active in soil during periods of flooding (paddy and delta soils). The most common type of the sulphate-reducing bacteria is *Desulfovibrio.*

III. TRANSFORMATION OF PHOSPHORUS COMPOUNDS BY MICROBIAL ACTIVITIES

(a) *Occurrence of phosphorus in the soil*

Phosphorus may occur in the soil in different compounds depending on type of soil, *pH*, organic matter content, etc. Most of these compounds are practically insoluble. Phosphorus deficiency of higher plants therefore is often due to the poor availability of the soil phosphorus rather than to an absolute shortage of this nutrient. This is particularly true of acid soils where a large part of the phosphorus is present as the ferric or aluminium compounds which are mostly very resistant to solubilization and, therefore, are poor sources of *P* supply to plants. In neutral or slightly alkaline soils a considerable part of the phosphorus may be present as finely precipitated di- and tricalcium phosphates. In such soils adequate amounts of phosphorus are rendered available from the soil phosphates, either by the activity of the plant roots themselves (excretion of carbon dioxide and eventually organic acids) or by soil microorganisms.

In many soils a relatively large part of the soil phosphorus is contained in organic compounds (nucleic acids, phospholipids, phytin, and still unknown compounds). Although the phosphorus of these compounds when the latter are applied in sterile media is readily available to higher plants, under soil conditions it may be highly unavailable as a result of fixation by inorganic soil constituents. This is particularly true of acid soils where insoluble ferric or aluminium compounds may be formed.

(b) *Effect of microorganisms*

Microorganisms may effect the solubilization of mineral phosphates in different ways: (i) by the formation of carbon dioxide and particularly of organic acids, (ii) by exerting a reducing effect on ferric phosphates which are converted to the more soluble ferrous compounds, (iii) by the production of hydrogen sulphide; this is a special case of (ii) and it also favours the solubility of phosphates.

(i) *Production of acids*

The solubilizing effect of microorganisms on a number of inorganic phosphates was clearly shown by Gerretsen (1948) in experiments with sand cultures of oat and mustard plants, either sterile or infected with a mixture of soil microorganisms. In the latter case considerably higher amounts of phosphorus were taken up by the plants. The effect of microorganisms was strongest when di- and tricalcium phosphates had been added to the sand. It apparently depended on the microbiological formation of organic acids from carbohydrates excreted by the plant roots as could be shown by using a special technique of plant growth.

From the results obtained Gerretsen concluded that the solvent action on mineral phosphate was not restricted to some typical organisms but would be due to several types of organisms. This conclusion is partly at variance with the suggestion of subsequent investigators that type of organic acid formed, and therefore type of organism, is important in explaining the beneficial effect of microorganisms on the solubilization of soil phosphates. According to these authors α-hydroxy acids and 2-ketoglucomiacid are important acids involved in the solubilization of soil phosphates (Sperber 1957; Duff, Webley and Scott 1963; Louw and Webley 1959a, b). So far no convincing evidence has been provided as to the importance of bacteria producing such acids for solubilizing soil phosphate under natural conditions. This is also true of the inoculation of soils with phosphate-dissolving bacteria (Mishustin and Naumova 1962).

(ii) *Reduced soil conditions*

When soils containing relatively large amounts of unavailable ferric phosphate are kept for a prolonged period of time under anaerobic conditions, solubility of the phosphate may be enhanced. This is a well known phenomenon in the culture of rice on flooded soils (Shapiro 1958a, b). In the presence of decomposable organic material, anaerobic degradation of this material decreases the redox potential of the soils which affects the reduction of the iron from the ferric into the ferrous state. This has a favourable effect on the solubility of the soil phosphate. Aluminium phosphate is slightly affected and tricalcium phosphate is not affected at all by anaerobic soil conditions.

(iii) *Formation of H_2S*

This represents a special case of (ii). It may be derived from sulphate by sulphate-reducing bacteria of the genus *Desulfovibrio* or from *S*-containing amino acids when exposed to anaerobic conditions.

IV. EFFECT OF MICROORGANISMS ON THE TRANSFORMATION OF SOME HEAVY-METAL-CONTAINING MINERAL FRACTIONS

Some of the most important microbial mineral transformations in nature are those concerning a number of heavy metal compounds (iron, manganese and to a smaller extent copper compounds). These heavy metals are required in small amounts (trace elements) by all types of living organisms in which they mostly function as co-factors in enzymatic reactions. Their availability to growing plants therefore is an important factor in soil fertility.

The transformations of iron and manganese in nature are more or less closely related. Both elements show a ready change in valency which affect a number of their properties, particularly their solubility. This valency change when occurring in soil or natural waters is often, but not always, a result of microbial activity.

(a) *Transformations of iron compounds in nature*

(i) *Oxidation of ferrous to ferric compounds*

This reaction often proceeds non-biologically. However, when the *pH* of the medium is below 5, oxidation proceeds only in the presence of certain types of autotrophic bacteria. These types of iron bacteria belong to the Thiobacillaceae (*Thiobacillus ferrooxidans, Ferrobacillus ferrooxidans*). They are very resistant to high concentrations of H^+ and heavy metals like Fe^{++} and Cu^{++}. They are found in media rich in ferrous salts (e.g. acid mine water) where masses of brown ferric hydroxide are formed.

A second type of iron bacterium belongs to the genus *Gallionella*. It is also a bacterium of slowly running water; it grows at neutral reaction and is thought to contribute to the oxidation of ferrous compounds under conditions of restricted oxygen supply (Kucera and Wolfe 1957).

A third type of bacteria implicated in the accumulation of large amounts of ferric hydroxide are the sheath-forming iron bacteria of the Chlamydobacteriaceae (*Leptothrix ochracea, L. discophora* etc.). These organisms require a *pH* of about 6-7 for growth. Under these conditions ferrous iron is readily oxidized non-biologically. Accumulation of large masses of flocculent ferric hydroxide is accomplished by the pronounced tendency of the bacteria to deposit this material on their sheaths (Mulder 1964; Mulder and van Veen 1963).

Although these three types of iron bacteria are common in iron-containing waters, evidence is available that also in soil microbial oxidation of ferrous iron may occur. This was clearly shown in experiments with acid soil of *pH* 3 by Gleen (1950). However, it may be expected that in neutral and alkaline soils ferrous iron is readily oxidized by a non-biological reaction.

(ii) *Reduction of ferric to ferrous iron*

This is undoubtedly a microbiological process which occurs when the soil is kept under anaerobic conditions (e.g. flooding). Microorganisms of various types may be assumed to contribute to the reduction process (Alexander 1961).

(iii) *Formation of ferrous sulphide*

Production of H_2S from sulphate by the anaerobic sulphate-reducing *Desulfovibrio desulfuricans* precipitates Fe^{++} as FeS. This compound may also be obtained when metallic iron is present in an anaerobic sulphate-containing medium (corrosion).

(b) *Transformation of manganese compounds in nature*

(i) *Non-biological oxidation of Mn^{++} to higher manganese oxides*

In contrast to Fe^{++}, Mn^{++} is practically not oxidized by non-biological processes at *pH* values common in most soils and natural waters. This type of manganese oxidation starts at *pH* values above 9. However, in the presence of relatively large amounts of hydroxycarboxylic acids (e.g. citrate, malate) Mn^{++} is oxidized non-biologically at about *pH* 8 to Mn^{+++} which as the citrate or malate is present as a brown solution. This phenomenon may be shown by placing small pieces of $NaHCO_3$ on agar plates containing 1% $MnSO_4$ and 2% *Ca* citrate or *Ca* gluconate (Söhngen 1914). A brown area of threevalent manganese will be formed surrounding the sodium bicarbonate. The inner part of the ring is often more darkly coloured, presumably due to the oxidation of the threevalent manganese to the fourvalent form (MnO_2) under the influence of the high salt concentration. This brown-black area of threevalent manganese citrate and MnO_2 is also formed by a large number of common soil organisms when streaked on the hydroxycarboxylic-acid-containing plates. Owing to the utilization of the hydroxycarboxylic acid by the bacteria, the *pH* rises to approximately 8 and this causes a non-biological oxidation of Mn^{++} to Mn^{+++} followed by precipitation of MnO_2.

Since the conditions required for this type of non-biological manganese oxidation (high concentrations of both Mn^{++} and hydroxycarboxylic acid) presumably do not occur in most soils, the process is thought to play no important part in the transformation of manganese in soil.

(ii) *Biological manganese oxidation by specific microorganisms*

The organisms involved in this type of manganese transformation include bacteria, fungi and yeasts. They are able to oxidize manganous compounds to manganic oxides (presumably MnO_2) at *pH* values as low as 6 and sometimes below 6.

Organisms of this type have been isolated as iron bacteria of the *Leptothrix* group from slowly running waters by several water microbiologists, including the present authors (Mulder 1964, Mulder and van Veen 1963).

Beijerinck (1913) isolated manganese-oxidizing bacteria and fungi from soil, and von Wolzogen Kühr (1927) obtained manganese-oxidizing bacteria from the filter beds of water works. Manganese oxidation by a mixture of two bacteria (a *Corynebacterium* sp. and a *Chromobacterium* sp.) has been recorded by Bromfield and Skerman (1950) and by Bromfield (1956). The former authors also studied three manganese-oxidizing fungi obtained from a manganese-deficient Australian soil. Zavarzin (1962/63) obtained manganese oxidation by a mixture of two *Pseudomonas* strains. Furthermore he described a manganese-oxidizing bacterium (*Metallogenium*) requiring the presence of a living fungus for growth and manganese oxidation (1964). Tyler and Marshall (1967a, b) isolated a manganese-oxidizing *Hyphomicrobium* from running lake water.

For the isolation and enumeration of manganese-oxidizing soil microorganisms $MnCO_3$-containing media were mostly used by the present authors. Fungi were isolated by a serial dilution technique or by streaking a very small amount of soil directly on a medium consisting of nutrient broth, 1; glucose, 1; $MnCO_3$, 1; oxoid agar, 7·5 g per liter of tap water. Zavarzin's manganese-acetate medium (1964) was also successfully used. To prevent the development of soil bacteria, 180 mg of chloramphenicol was added per l of these media. The growth of fungi and the oxidation of Mn^{++} were practically not affected by this concentration of the antibioticum.

For bacteria and fungi a medium consisting of $(NH_4)_2SO_4$, 0·5; K_2HPO_4, 0·05; KCl, 0·05; $MgSO_4 \cdot 7H_2O$, 0·05; $CaCO_3$, 0·1; $Ca(NO_3)_2$, 0·01; glucose 0·15 and oxoid agar, 10 g per liter of tap water was used.

A central hole, about 2 cm wide, containing a suspension of $MnCO_3$, supplied the agar medium with small amounts of Mn^{++}. In this way the agar kept its transparency so that microscopical observations could be made. To prevent drying up of the plates during the prolonged incubation period sterile water was periodically added to the central core.

For the enumeration of manganese-oxidizing bacteria in soil, samples were taken from sandy soils with different *pH* present in the garden of the Laboratory of Microbiology at Wageningen. These plots showed a wide variation in plant-available manganese resulting from the differences in acidity. Colonies of fungi were counted after a 4 to 5 days' incubation period at 25°C, those of bacteria after an incubation period of three weeks. Large numbers of manganese-oxidizing bacteria and fungi were counted in both neutral and acid soils. A soil of *pH* 7 for instance gave about $4 \cdot 10^3$ colonies of manganese-oxidizing fungi per g of soil tested; for manganese-oxidizing bacteria numbers as high as 10^6 per gram of soil were found. Although soils of *pH* 5 gave somewhat higher values for fungi, bacterial numbers were only slightly lower. This demonstrates that in soil no correlation exists between number of manganese-oxidizing microorganisms, and state of oxidation of the soil manganese. Since the latter is correlated with the *pH* of the soil, the highest values being found between *pH* 6·5 and 8, the manganese-oxidizing ability of the microorganisms might be correlated with the *pH* of their medium. This hypothesis was confirmed by the results of experiments with washed fungal cells. Optimal manganese-oxidizing activity was found at *pH* 7·0. To both sides the *pH*-manganese-oxidation-curve readily dropped so that no oxidation occurred below *pH* 5·0 and above *pH* 8·5. Indications were obtained that bacterial cells behave in a similar way.

Among the fungi frequently isolated from soil *Coniothyrium fuckelii* Sacc. and *Phoma eupyrena* Sacc.* were found to be strong manganese oxidizers. *Cryptococcus albidus* is a manganese-oxidizing yeast and *Hypomicrobium* a stalk-forming manganese-oxidizing bacterium occurring in large numbers in the soil of the laboratory garden. The observation that *Hyphomicrobium* is an important representative of the manganese-oxidizing bacteria, is in agreement with the finding of Tyler and Marshall (1967a, b) that this organism is responsible for the formation of manganese-rich deposits in hydro-electric pipelines in Tasmania. In addition to *Hypho-*

---

* Identified by Centraalbureau Schimmelcultures, Baarn, Netherlands.

microbium, a considerable number of unidentified manganese-oxidizing bacteria were isolated from the garden soil.

(iii) *Role of microorganisms in rendering soil manganese unavailable*

There is no agreement among research workers as to the effect of microorganisms in rendering soil manganese unavailable to plants. Microbiologists usually believe that microbial formation of manganic oxides is the main cause of the decreased availability of the manganese when added in the bivalent form to neutral or slightly alkaline soils containing a certain amount of organic matter.

Some authors are of the opinion that fixation of Mn^{++} by soil organic matter is the main reason for its unavailability.

To demonstrate that biological transformation of Mn^{++} plays an important part in rendering added manganese insoluble, samples of a neutral sandy soil supplied with 114 mg Mn in the form of $MnSO_4$ per 100 g soil were exposed to toluene-chloroform or to water vapour. Water-soluble as well as versenate-acetate-soluble manganese (Beckwith 1955) were estimated after different periods of time. In addition manganese-oxidizing bacteria and fungi were determined. After a 4 months' incubation period all the added manganese of the untreated soil had become insoluble as contrasted with 12 per cent in the toluol-chloroform-treated soil. After 2 months' incubation these values were 70 and 13% and after 3 weeks, 26·5 and 11·4%, respectively. Manganese-oxidizing fungi had almost entirely disappeared by the toluene-chloroform treatment, while the manganese-oxidizing bacteria also showed a serious drop in number.

(iv) *Reduction of manganic to manganous compounds*

Reduction of MnO_2 in soil is a biological process. Several microorganisms which decompose organic matter can apparently use MnO_2 instead of oxygen as H acceptor, reducing it to Mn^{++} (Man and Quastel 1946).

MnO_2 can furthermore be reduced to Mn^{++} by certain compounds formed by microbial processes, e.g. H_2S.

The biological reduction of manganic oxides is strongly favoured by a drop in soil pH to a value below 5·5.

Roots of living plants may promote the solubilization of MnO_2 by excreting organic acids or other compounds stimulating bacterial activity (rhizosphere effect).

(c) *Effect of microorganisms on transformation of copper compounds in soil*

Although the availability of copper in soils is often related with the presence of black organic humus compounds, activity of microorganisms may sometimes interfere with the copper supply of higher plants.

(i) *Copper precipitation by hydrogen-sulphide-producing bacteria*

Two types of H_2S-forming microorganisms may be involved in copper precipitation (Mulder 1938, 1939). The first type includes bacteria producing H_2S from sulphur-containing amino acids and peptides (cystine, methionine, glutathion, etc.). Proteolytic clostridia, *Proteus vulgaris, Escherichia coli* etc. belong to this group. The second type includes the sulphate-reducing bacteria. Both types of H_2S-forming bacteria were found to precipitate Cu in such a form (CuS or some other S compound) that it was unavailable to higher plants and to *Aspergillus niger* used as test organisms. Since purely chemically produced CuS was a good copper source for both test organisms, it must be assumed that copper precipitated by H_2S-forming bacteria is more resistant to solubilization than non-biologically precipitated CuS. This may be due to concentration of the copper sulphide on or within the bacterial cells which protects it from oxidation.

Since microbial H_2S-formation may occur in natural soils and peats under anaerobic conditions (water logging), this process in certain soils is thought to be responsible for the poor copper supply of the plants.

(ii) *Solubilization of copper sulphide by microorganisms*

Bacteria of the genera *Thiobacillus* and *Ferrobacillus* are able to oxidize CuS to $CuSO_4$ (Bryner and Jameson 1958). These bacteria can resist very high concentrations of Cu^{++} (10,000 to 20,000 ppm as contrasted to 0·5 ppm in heterotrophic bacteria: Booth and Mercer 1963, Mulder 1938, 1939).

V. REFERENCES

Alexander, M. (1961)—"Introduction to soil microbiology." (John Wiley and Sons, Inc., New York, London).

Beckwith, R. S. (1955)—*Aust.J.agric.Res.* **6**, 299-307.

Beijerinck, M. W. (1913)—*Folia microbiol.Delft* **2**, 123-134.

Booth, G. H. and Mercer, S. J. (1963)—*Nature, Lond.* **199**, 622.

Bromfield, S. M. (1956)—*Aust.J.biol.Sci.* **9**, 238-252.

Bromfield, S. M. and Skerman, V. B. D. (1950)—*Soil Sci.* **69**, 337-348.

Bryner, L. C. and Jameson, A. K. (1958)—*Appl.Microbiol.* **6**, 281-287.

Duff, R. B., Webley, D. M. and Scott, R. O. (1963)—*Soil Sci.* **95**, 105-114.

Gerretsen, F. C. (1948)—*Pl.Soil* **1**, 51-81.

Gleen, H. (1950)—*Nature, Lond.* **166**, 871-872.

Kucera, S. and Wolfe, R. S. (1957)—*J.Bact.* **74**, 344-349.

Louw, H. A. and Webley, D. M. (1959a)—*J.appl.Bact.* **22**, 216-226.

Louw, H. A. and Webley, D. M. (1959b)—*J.appl.Bact.* **22**, 227-233.

Mann, P. J. G. and Quastel, J. H. (1946)—*Nature, Lond.* **158**, 154-156.

Mishustin, E. N. and Naumova, A. N. (1962)—*Mikrobiologiya* **31**, 543-555; Eng. transl. *Microbiology* **31**, 442-452.

Mulder, E. G. (1938)—"The importance of copper for the growth of plants and micro-organisms" (in Dutch). Thesis, Wageningen.

Mulder, E. G. (1939)—*Arch.Microbiol.* **10**, 72-86.

Mulder, E. G. (1964)—*J.appl.Bact.* **27**, 151-173.

Mulder, E. G. and van Veen, W. L. (1963)—*Antonie van Leeuwenhoek* **29**, 121-153.

Shapiro, R. E. (1958a)—*Soil Sci.* **85**, 190-197.

Shapiro, R. E. (1958b)—*Soil Sci.* **85**, 267-272.

Silverman, M. P. and Ehrlich, H. L. (1964)—*Adv.appl.Microbiol.* **6**, 153-206.

Söhngen, N. L. (1914)—*Zentbl.Bakt.ParasitKde.* Abt II 40, 545-554.

Sperber, J. I. (1957)—*Nature, Lond.* **180**, 994-995.

Starkey, R. L. (1966)—*Soil Sci.* **101**, 297-306.
Tyler, P. A. and Marshall, K. C. (1967a)—*Antonie van Leeuwenhoek* **33**, 171-183.
Tyler, P. A. and Marshall, K. C. (1967b)—*Arch.Mikrobiol.* **56**, 344-353.
Wolzogen Kühr, C. A. H. von (1927)—*J.Am.Wat.Wks Ass.* **18**, 1-31.
Zavarzin, G. A. (1962)—*Mikrobiologiya* **31**, 586-588; Eng. transl. *Microbiology* **31**, 481-482.
Zavarzin, G. A. (1964)—*Z.allg.Mikrobiol.* **4**, 390-395.

SUMMARY

An assessment of microbial transformations of sulphur and phosphorus compounds is followed by a more detailed examination of transformations of iron, manganese and copper.

Sulphur transformations are implicated in many changes, for hydrogen sulphide can act both as hydrogen donor for reduction of minerals and as energy source. Hydrogen sulphide formed by sulphate reduction under anaerobic conditions can increase the solubility of ferric phosphates, other ferric salts and manganic oxides by chemical reduction and can precipitate copper sulphide in a highly resistant form. Ferric salts, manganic oxides and insoluble phosphates can also be solubilized in soil by microbial production of reducing conditions and organic acids.

Oxidation of ferrous and manganese salts to insoluble compounds can occur both microbiologically and non-microbiologically. Although non-biologic ferrous ion oxidation can occur above *pH* 5, such oxidation of manganese commences at *pH* 8 to 9 and is thus likely to be of only limited occurrence naturally. Large numbers of manganese-oxidizing bacteria and fungi have been isolated from neutral and acid soils. There was no correlation between numbers of manganese oxidizers and the state of soil manganese. Mangenese oxidation by washed fungal cells occurred between *pH* 5 and 8·5 with a marked optimum at *pH* 7. In a neutral sandy soil, microbial oxidation of manganese was much more important in rendering manganese insoluble than was possible fixation by soil organic matter.

RÉSUMÉ

Un exposé des transformations microbiennes des complexes de soufre et de phosphore est complété par un examen plus détaillé des transformations de fer, manganèse et cuivre.

Les transformations de soufre sont impliquées dans plusieurs changements car l'hydrogène sulfuré peut agir à la fois comme réducteur des minéraux et comme source d'énergie. L'hydrogène sulfuré, formé par la réduction de sulfate sous des conditions anaérobies, peut augmenter la solubilité des phosphates ferriques, autres sels ferriques et oxydes de manganèse par réduction chimique, et peut précipiter le sulfure de cuivre sous une forme très résistante. Les sels ferriques et les oxydes de manganèse ainsi que les phosphates insolubles peuvent également être solubilisés dans le sol par la production microbienne des conditions de réduction et des acides organiques.

L'oxydation des sels ferreux et des sels de manganèse en combinaisons insolubles peut se produire microbiologiquement et non-microbiologiquement. Quoique l'oxydation non-biologique des ions ferreux peut se produire au-dessus du *pH* 5, une telle oxydation de manganèse commence au *pH* 8-9 et par conséquent il semble que son occurrence naturelle est limitée. Un grand nombre de bactéries et de champignons oxydant le manganèse a été isolé des sols neutres et acides. Il n'y avait pas de corrélation entre le nombre d'oxydants de manganèse et l'état du manganèse du sol. L'oxydation du manganèse par des cellules fongiques lavées se produisit entre *pH* 5 et 8,5, atteignant le maximum à *pH* 7. Dans un sol sableux neutre l'oxydation microbienne du manganèse était beaucoup plus importante pour rendre le manganèse insoluble qu'une fixation possible par les matières organiques du sol.

ZUSAMMENFASSUNG

Nach einem kurzen Bericht über die mikrobiologischen Veränderungen der Phosphor- und Schwefelverbindungen folgt eine ausführliche Untersuchung der Veränderungen des Eisens, des Mangans und des Kupfers.

Schwefelveränderungen sind in vielen Wandlungen einbegriffen, da der Schwefelwasserstoff zugleich als Reduktionsmittel der Mineralien und auch als Energiequelle wirken kann. Der durch Sulfatreduktion unter anaeroben Verhältnissen gebildete Schwefelwasserstoff, kann die Löslichkeit der Ferriphosphate, andere Ferrisalze und Manganoxyde durch chemische Reduktion steigern, und kann Kupfersulfid sehr widerstandsfähig fällen. Ferrisalze und Manganoxyde sowie unlösliche Phosphate können auch im Boden gelöst werden und zwar mittels mikrobiologischer Bildung von Reduktionsverhältnissen und organischen Säuren.

Die Oxydation der Ferro- und Mangansalze zu unlöslichen Salzen und Oxyden kann sich sowohl mikrobiologisch als auch nicht-mikrobiologisch ereignen. Obwohl die nicht-biologische Eisen-ionenoxydation bei über *pH* 5 stattfindet, beginnt eine solche Oxydation des Mangans erst bei *pH* 8 bis 9, und kann daher nur selten in der Natur vorkommen. Eine grosse Anzahl von Mangan oxydierenden Bakterien und Pilzen wurde in neutralen und sauren Böden isoliert. Man fand keine Korrelation zwischen der Zahl der Manganoxydierenden Mikroorganismen und dem Zustand des Bodenmangans. Die Manganoxydation durch ausgewaschene Fungizellen fand bei *pH* 5 bis 8·5 statt, mit einem optimum bei *pH* 7. In einem neutralen sandigen Boden war die mikrobiologische Manganoxydation viel wichtiger, um das Mangan unlöslich zu machen, als eine mögliche Fixierung durch organische Substanzen.