The Mechanism of Reduction in Paddy Soil

By YASUO TAKAI

Professor, Department of Agricultural Chemistry,
Faculty of Agriculture, University of Tokyo

Japan's research on paddy soil in post-war period has clarified that the fertility of paddy soil is largely controlled by its ability to supply plant nutrient and its oxidation-reduction condition as environmental factor of root. This paper intends to discuss the development process of reduction condition in paddy soil from the viewpoint of microbial metabolism with the focus on research findings of Takai *et al.*

It is a well-known fact that, in the case of flooded paddy soil, because the oxygen supply from atmosphere is shut off by surface water, the reduction advances in accompaniment with the consumption of oxygen by the decomposition of organic matter.

First, the study is directed to the consumption condition of oxygen. When paddy soil is submerged under laboratory condition, the oxygen is completely lost within 24 hours.1), 2) In the case of paddy soil3) submerged into Wagner's pot under green house and of the same soil4) under the flooded field condition, the oxygen has disappeared in a few days and notwithstanding the supply of dissolved oxygen in accompaniment with the diffusion and water percolation thereafter no oxygen has been detected in soil for the duration of submergence. The oxygen has been discovered only during the mid-summer drainage. The result in measuring O_2 uptake of submerged paddy soil by using Warburg's manometer has clarified that a major portion of O_2 uptake of submerged paddy soil is dependent on microbial metabolism in early submerged period but the same uptake in late period is dependent not only on microbial metabolism but on the autooxidation of the ferrous, etc. From the above results it is assumed that in submerged paddy soil the oxygen is rapidly utilized by microbe-s during early submerged period and the supply of oxygen thereafter is immediately lost by microbial metabolism of soil's very top layer and by autooxidation of reduced materials.

As for the nitric acid, in paddy soil submerged both under laboratory condition and in Wagner's pot a major portion thereof has disappeared in 24 hours or 2~3 days.2), 3) Whether or not there was any water percolation during the submergence, practically no accumulation of nitric acid and nitrous acid has been recognized since then. Only small volume of nitric acid has been discovered immediately after the mid-summer drainage. Thus, it is assumed that nitric acid reduction advances during early period after the flooding of paddy soil.

In parallel with the above changes or perhaps immediately thereafter, the ferrous formation actually progressed in submerged paddy soil. The change in Eh and pH has emerged in parallel with ferrous formation, clarifying the fact that ferric-ferrous system controls the Eh to large extent.

In the course of the disappearance of oxygen and nitric acid and also of the progress in ferrous formation, ammonium and carbon dioxide have formed remarkably,2), 3) but organic acids which is the intermediate of anaerobic decomposition, i.e. the fermentation of soil organic matters by microbe did not emerge or was not remarkable.

When Eh remarkably declined caused by the advance in ferrous formation, the sulfide and methane have emerged. The hydrogen gas which is a fermentation product has emerged within 24 hours of early submerged period when easily decomposable organic matters, particularly soluble sugars existed in large quantity, but it has disappeared within 48 hours.6),7) Since then from the same time of methane emergence a few volume of hydrogen has been found. Organic acid has accumulated in large quantity when Eh declined to certain extent, but afterward, along with the active methane formation it declined remarkably. Major organic acids in submerged paddy soil were lower fatty acids such as acetic, formic and butyric, among which the acetic was by far the largest.2),3),4) Two metabolic pathways in submerged paddy soil leading from fatty acids to methane are shown by the istopic analysis8) using ^{14}C tracers. One is the reduction carbon dioxide, fatty acids with more than 2 carbon atoms being used as hydrogen acceptor ($^{14}CO_2 + 4H_2A \rightarrow {}^{14}CH + 2H_2O + 4A$). The other is transmethylation of accetic acid ($^{14}CH_3COOH \rightarrow {}^{14}CH_4 + CO$).

When the above chemical transformation is compared with microbial counts by culture method, the increase in microbial counts of aerobic and facultative anaerobic bacteria emerges most orderly with early disappearance of oxygen and nitric acid and also with ferrous formation. After the first step, when Eh has dropped, the increase of counts of anaerobic bacteria by deep tube method and sulfate reducers occurs in parallel with the accumulation of organic acids and the formation of sulfide and methane.

From the deduction based upon the above findings and in the light of microbial physiology, the course of microbial metabolism concerned with the reduction in submerged paddy soil can be classified into two stages: namely, the stage where aerobic and facultative anaerobic bacteria oxidatively decompose the organic matters with oxygen, nitric acid and ferric as hydrogen aceptor and the stage where obligate anaerobes such as sulfate reducer and methane bacteria work.

This paper intends to study in detail the content of the first stage of reduction course which has been classified by the writer into two stages.

The cell needs energy for the synthesis of new materials and for staying alive. It obtains this energy by biological oxidation - respiration in a wider sense - of substrates. Among the various kinds of energy-yielding reactions, the most efficient is aerobic respiration with oxygen, respiration in the absence of oxygen being less efficient. It has been known that the former requires molecular oxygen as an hydrogen acceptor, while the latter requires nitrate, sulfate, carbon dioxide or oxygen-rich organic compounds such as pyrurate and acetate.

Accordingly, it is assumed that, soon after flooding, oxygen and nitrate in paddy soil are utilized as hydrogen acceptors in microbial respiration, aerobic respiration proceeding first and being followed by nitrate-reducing respiration.

In addition to oxygen and nitrate, the soil contains the other kinds of oxidizing agents such as easily reducible manganese oxide and free iron oxide. The amounts of these elements in a typical paddy soil is shown below, expressed in terms of ml O_2 per 100 g of over-dry soil: molecular oxygen 2.4 ml, nitrates 0.6 ml, manganese oxide 4.3 ml, ferric 56.0 ml. When this soil was incubated at 20°C under submerged condition, manganous ion was formed first and, after this reduction process

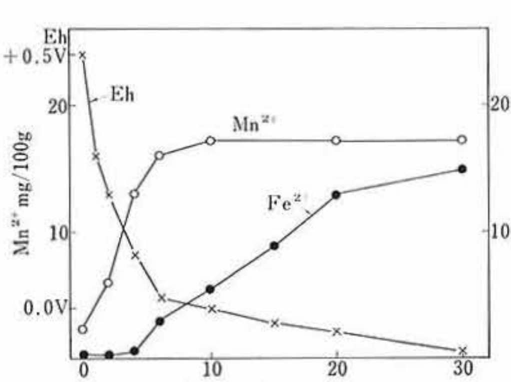

Fig. 1. Successive reduction of manganese and iron.

has almost stopped, ferrous formation began (Fig. 1). The decline of Eh went on in parallel with the formation of manganous and, thereafter, of ferrous.

When a soil with a high content of manganese oxide was incubated at 20°C under submerged condition, a phenomenon was observed in which the addition of nitrate retarded the start of manganese reduction (Fig. 2).

From the above results it can be reasonably concluded that the stepwise reduction of oxidizing agents in the submerged soil, starting from oxygen and nitrate respiration through manganese reduction to ferric reduction has been established.

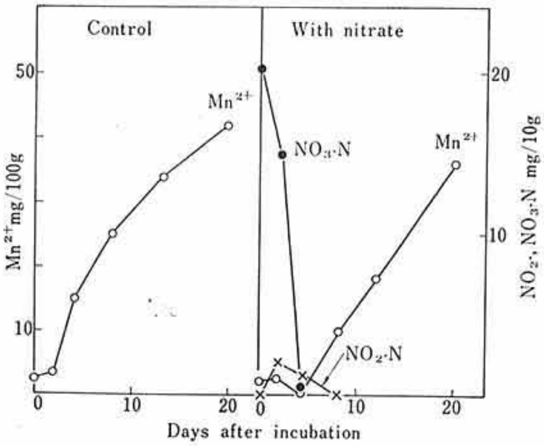

Fig. 2. Repression of manganese reduction following the addition of nitrate

Because, among these oxidizing agents, ferric surpasses by far the other ones in quantity, the relationship between ferric reduction and microbiol metabolism was studied in detail.7), 9) The results of our experiments suggested the possibility that ferric reduction occurs linked with an energy producing reaction of soil microbes. It has been shown that organic acids such as acetic were oxidatively decomposed to carbon dioxide coupled with ferric reduction by the following pathway:

$CH_3COOH + 8Fe(OH)_3 \rightarrow 2CO_2 + 8Fe(OH)_2 + 6H_2O$. The addition of hydrous iron oxide retarded significantly methane formation in submerged paddy soil.

These results lead us to outline the sequence of microbial metabolism in reduction process as is given in Table 1. It is assumed that the type of microbial metabolism in submerged paddy soil changes successively from aerobic respiration in the presence of molecular oxygen, which is the most efficient energy-yielding reaction ($-\Delta F$ 56 Kcal), through nitrate reduction ($-\Delta F$ 53∼36 Kcal) *et al.* to methane fermentation, which is a very inefficient energy-yielding reaction ($-\Delta F$ 9.2∼6.7 Kcal).

Which stage in reduction process, given in Table 1, surpasses another stage during sub-

Table 1. Successive reduction process in submerged paddy soils

Period of incubation	Stage of reduction	Chemical transformation	Initial Eh in soil V	Expected pattern of energy metabolism	Formation of NH_4-N	Formation of CO_2	Formation of organic acids	Hypothetical pattern of organic matter decomposition
Earlier	The 1st stage	Disappearance of molecular oxygen Disappearance of nitrate Formation of Mn^{2+} Formation of Fe^{2+}	+0.6∼+0.5 +0.6∼+0.5 +0.6∼+0.4 +0.6∼+0.3	Oxygen respiration Nitrate reduction (Manganese reduction) (Ferric reduction)	Rapid progress	Rapid progress	No accumulated or a few amount accumlated	Aerobic and semi-anaerobic decomposition process
Later	The 2nd stage	Formation of sulphide Formation of hydrogen Formation of methane	0 ∼−0.19 −0.15∼−0.22 −0.15∼−0.19	Sulphate reduction Fermentation Methane fermentation	Slow progress	Slow progress	Early stage: rapid Accmulation Advanced stage: rapid decrease	Anaerobic decomposition process

mergence, depends largely both on the reducible ferric content, that is oxidizing power, and on the easily decomposable organic matter content, that is reducing power.²⁾ When the former surpassed the latter, the 1st stage of reduction process progressed longer than the 2nd stage during submergence. When the latter surpassed the former, the 2nd stage began to occur earlier, and progressed considerably. The comparison between the soil with a lower content of organic matter and that with a higher content of organic matter, of which reducible ferric content are about

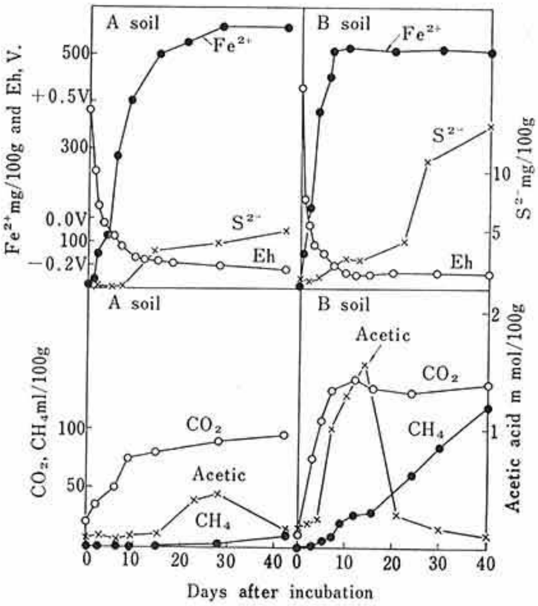

Fig. 3. Reduction process under submerged condition in A soil with a low content of organic matter and in B soil with the higher content.

the same, is given in Fig. 3. In the former A soil the 1st stage made progressed for a longer period, while in the latter B soil the 2nd stage progressed more violently than in the former.

Such successive reduction process with reference to manganese, iron and sulfate was established in paddy soil under field condition in situ.¹⁰⁾

References

1) Takai, Y., Koyama, T. and Kamura, T.: Microbiological Studies on the Reduction Process of Paddy Soils. Trans. Intl. Soc. Soil Sci. 527, 1956.
2) Takai, Y., Koyama, T. and Kamura, T.: Effect of Iron and Organic Matter on The Reduction Process in Paddy Soils (1) Soil Sci. & Plant Nutrition, 9, 10. 1963.
3) Takai, Y., Koyama, T. and Kamura, T.: Effact of Rice Root and Water Percolation on the Reduction Process in the Paddy Soil Submerged into Wagner's pot. J. Sci. Soil Manure, Japan, 40, 15. 1969. (In Japanese).
4) Takai, Y. and Koyama, T.: Composition of Gases and Organic Acids Contained in Soil of Paddy Field. J. Sci. Soil Manure, Japan, 26, 509. 1956. (In Japanese).
5) Takai, Y., Kamura, T. and Adachi, T.: On the Behavior of Iron Compound in Paddy Soils. J. Sci. Soil Manure, Japan ,29, 216. 1958. (In Japanese).
6) Yamane, I and Sato, K.: Initial Rapid Drop of Oxidation-reduction Potential in Submerged Air-dired Soils. Soil Sci. & Plant Nutrition, 14, 68. 1968.
7) Asami, T., and Takai, Y.: Behaivor of Free Iron Oxide in Paddy soils, Part 4. Relationship Between the Reduction of Free Iron Oxide and the Formation of Gases in Paddy Soils. J. Sci. Soil Manure, Japan, In press. 1969. (In Japanese).
8) Takai, Y.: The Mechanism of Methane Fermentation in Paddy Soil. Soil Sci. & Plant Nutrition, In press 1969.
9) Taki, Y.: Microbiological Mechanism of ferric reduction in Paddy Soils. J. Sci. Soil Manure, Japan. 32, 135. 1961. (In Japanese).
10) Gotoh, S. and Yamashita, K.: Oxidation-reduction Potential of a Paddy soil in situ with Special Reference to the Production of Ferrous Iron, Manganous Manganese and Sulfide. Soil Sci. & Plant Nutrition. 12, 230. 1966.