d. The development of these layers of hydrated ferric hydroxide deposit can be explained by the principles used to explain the Liesegang phenomenon. For the sake of simplicity, consideration is given to the case where there is no downward movement of water. When the reduced soil beneath the oxidized layer is oxidized by the oxygen diffusing downward from the surface water, its pH first is lowered; then, its ferrous compounds, probably precipitated ferrous sulfides and some other ferrous compounds, become soluble in such forms as ferrous sulfate and probably ferrous bicarbonate. The soluble ferrous ions diffuse upwards into the more highly oxidized layer. In this layer the diffused ferrous ions are oxidized to the ferric form and precipitate out by hydrolysis as hydrated ferric hydroxide. Thus, immediately below this layer of hydrated ferric hydroxide deposit is a bleached layer of one to two millimeters in thickness with little oxidizable substances through which oxygen diffuses downward quite easily. Below this bleached layer another layer of ferric hydroxide and a bleached layer are produced by the same processes.

e. To elucidate further the profile development of paddy soils under flooded conditions, the experiments presented in Table 3 and 4 were carried out. The soils used in these experiments were obtained on 15 December 1940 from the furrow slice of paddy fields and upland fields of the Agricultural Experiment Station, Konosu, Saitama Prefecture. a/ In one series the samples were flooded and incubated without air-drying, and in the other series the samples were air-dried prior to flooding and then were incubated. A sample corresponding to 200 g of air dried soil was placed in a 250 cc beaker (depth of soil was 7 cm), covered with distilled water to a depth of about one centimeter, and incubated at 26° C and left undisturbed until the time of analysis. The following methods of analysis were used; b/

(1) pH of soil --------- Quinhydrone method

(2) Eh of soil --------- Brown's method

(3) Total nitrogen in the absence of nitrate-nitrogen, Kjeldahl method; in the presence of nitrate-nitrogen, Forster's method. 15/

(4) Ammonium-nitrogen ------ Harper's method 13/

(5) Nitrate-nitrogen ------ Harper's method 12/

(6) Exchange acidity of the wet soil was determined in the following manner. To the wet soil a calculated amount of KCl solution was added so that a ratio of 250 cc of 1N KCl solution for every 100 g of air dry soil was obtained. After shaking one hour, 125 cc of supernatant solution was taken and after boiling titrated with N/10 NaOH solution using phenolphthalein as indicator. The number of cubic centimeters of N/10 NaOH used for neutralisation of 125 cc of supernatant KCl solution is designed as Y_1.

f. The results are summarized as follows.

(1) Air drying of the soil samples resulted in an increase in ammonium-nitrogen, pH, and exchange acidity of wet soil. A decrease in Eh resulted after the samples were flooded and incubated. These trends were especially marked in the samples from paddy fields and were not characteristic of the sample from upland soils. Sample C from the upland field which was not fertilized yearly was particularly lacking in such characteristics.

(2) After the samples were flooded, except for certain observations of sample C from an upland field, a rice in pH and exchange acidity of wet soil and a decrease in Eh resulted. Since the ammonium-nitrogen content of the samples was determined after only 33 days of flooding, the amount of its quantitative changes was not determined fully in this experiment. However, as will be shown later, the ammonium-nitrogen content of the soil increases after flooding and, at constant temperature, attains its maximum amount within two or three weeks.

(3) In the samples from paddy fields, the differentiation of the reduced layer and the oxidized layer was clearly observed 14 days after flooding the air-dried samples and 33 days after flooding the non-air-dried samples.

The samples of upland soils did not develop a reduced layer and remained in an oxidized condition even after flooding.

(4) The Eh values of the oxidized layers of the soil samples were greater than +0.3 volt. expressed as E_6. This critical redox-potential of the oxidized layer has been confirmed by many other experiments conducted by the writer and his associates.

(5) The pH values of the oxidized layer were lower than that of the reduced layer for each respective sample.

(6) Analysis made 33 days after flooding showed that the oxidized layer of paddy soils contained considerably less ammonium-nitrogen than that of the reduced layer.

(7) The exchange acidity of wet soil, designated Y_1 corresponds roughly to the amount of Fe^{++} extracted from the soil by K in exchange reaction. 21/ Hence, it may be assumed from Y_1 of the respective soils that the oxidized layer contains much less exchangeable Fe^{++} than the reduced layer.

(8) A high pH Value accompanied by a high Y_1 value shows that the increase of Y_1 indicates a lowering of real soil acidity.

(9) Large amounts of sulfides were found in the reduced layer of the samples from paddy fields but not in the oxidized layer. The presence of sulfides was not clearly observed in the samples from upland fields.

g. The results summarized in the preceding paragraphs are in agreement with the results obtained by Pearsall and Mortimer. 17/ These investigators concluded from a study of natural waters, waterlogged soils and muds that the critical value of Eh between conditions of oxidation and of reduction is approximately +0.35 volt expressed as E_5, and that stable forms of inorganic compounds of nitrogen, sulfur, and iron are present as NO_3^-, $SO_4^{=}$, and Fe^{+++} in the oxidized layer and as NH_4^+, S^{--}, and Fe^{++} in the reduced layer.

h. To explain the reaction of rice soil it is desirable to study the basicity of Fe^{++}, Al^{+++}, and Fe^{+++}. Britton[4] has studied the relationship between pH and the precipitation of hydroxides of many metallic ions from solution. His results show that if the acidified solutions of salts are neutralized with NaOH solution, Fe^{++} begins to precipitate out at pH 5.5 and Al^{+++} at pH 4.1, while Fe^{+++} assumes the colloidal form at pH 2-3. From these results, it can be concluded that Fe^{+++} does not enter into the exchange acidity of acid soils. If a well-oxidized acid soil is treated with a solution of neutral salt such as KCl, the soil colloids absorb the positive ion, in this case K^+, and release H^+ to the solution by exchange reaction. The solution soon becomes acid enough to keep aluminium chloride in solution and the Al is replaced from the soil colloids by K^+. The soil solution then is changed into a buffer solution with a pH of approximately 4.1 and containing KCl and $AlCl_3$. The Al^{+++} in soil colloids inhibits the replacement of Fe^{+++} by K^+, because of the strong attraction of Fe^{+++} for OH^- as compared to Al^{+++}. However, if Fe^{+++} is reduced to Fe^{++} in a more or less unstaurated soil, the circumstances are changed. 6/ Fe^{++} is replaced, for instance, by K at the weakly acidic reaction. The solution becomes a buffer solution at a pH of approximately 5 or at a slightly higher pH and contains $FeCl_2$ and KCl. In this way a reduced soil often shows a high "exchange acidity of wet soil". As is mentioned above, however, an increase in this exchange acidity promoted by a process of reduction means a decrease of soil acidity as defined by pH. 21/

i. Air-drying of paddy soil not only promotes ammonium-nitrogen formation, but it also increases the availability of phosphoric acid. At Kyoto Imperial University Aoki concluded that the effective part of the phosphoric acid in paddy soils appears to be present as iron compounds, and their solubility seems to be increased by conditions of reduction. 2/ The results of a pot experiment given in Table 5 show that air drying of paddy soil before transplanting markedly increases the availability of phosphoric acid as well as nitrogen. 25/ Under a flooded condition, the phosphoric acid combined with the free ferric hydroxide changes to ferrous phosphate. This change is especially great where the soil was air-dried beforehand. The phosphate will be dissolved by the acid solution at the periphery of the roots of rice plants. The acid reaction can be due to acids excreted by the roots and produced by an oxidation process of the roots.

5. Denitrification in flooded soil 22/

a. Relationship between denitrification and depth of soil layer.

(1) Paddy soils kept under water develop an oxidized layer and a reduced layer. If the differentiation of the oxidized layer gives rise to denitrification, it is believed that a deep soil will contain less ammonium-nitrogen than a shallow soil. This belief was tested in the experiments presented in Table 6. The results are in agreement with this supposition.

b. Denitrification in flooded soil and the influence of soil reaction.

(1) Observations have been made that ammonium-nitrogen, applied in the forms of ammonium sulfate or ammonium chloride to a certain soil, did not decrease under flooded condition. The cause of this peculiar behavior is believed due to the acid reaction of the soil in the oxidized layer. To confirm this belief, the experiment summarized in Table 7 was conducted using the same soil.

(2) The reactions of the samples were determined 50 days after flooding. The soil samples to which were added $(NH_4)_2SO_4$ or Na_2SO_4, with or without phosphates, showed a highly acidic reaction in the oxidized layer but not in the reduced layer where the reaction was slightly basic. The samples which had phosphates alone showed weakly acidic or neutral reaction in the oxidized layer. The reaction of the oxidized layer in the check sample was basic.

(3) The loss of nitrogen during the 50 days of flooding the soil was determined in the check samples. This also was done for the sample that received $(NH_4)_2SO_4$ and for the sample treated with $(NH_4)_2HPO_4$. The loss of nitrogen was confirmed in the sample that had $(NH_4)_2HPO_4$, but no loss occurred in the sample to which was added $(NH_4)_2SO_4$. The check sample also showed no loss of nitrogen.

(4) The loss of ammonium-nitrogen added to the sample was influenced by the nature of other materials added. Sulfates tended to decrease strongly the loss of ammonium-nitrogen applied in the form of phosphates. The order of loss coincided well with the order of the pH values of the soil in the oxidized layer of the samples. It seems that a high pH value in the oxidized layer results in a loss of ammonia-nitrogen directly to the air or indirectly as nitrogen gas.

c. Formation of nitrogen gas through denitrification in a flooded soil. 19/

(1) Whether the loss of nitrogen from flooded soil is from the nitrification of ammonium-nitrogen and its subsequent denitrification or from the evaporation of ammonia due to the alkaline reaction of the soil cannot be ascertained in the experiment mentioned in the preceding paragraphs (section 5-6a). Sreenivasen and Subrahmanyan have stated that loss of nitrogen by the latter process occurred in a flooded soil to which materials of a low carbon: nitrogen ratio were added. 30/

From preliminary investigations made by the writer and his associates, however, it can be said that loss of nitrogen from flooded paddy soils results largely because of denitrification. 23/

(2) To prove that denitrification occurs in flooded soils, the following experiment was carried out using soil samples taken from a paddy field at the Agricultural Experiment Station, Konosu, Saitama Prefecture. Wet soil equivalent to 30 grams of dry soil was placed in bottles of 250 cc capacity. To one sample 10 mg of nitrogen was added in the form of ammonium sulfate. No nitrogen was added to the check sample. Enough distilled water was added to cover the soil samples. Air in the bottles then was replaced with oxygen gas, the bottles were sealed with paraffin and incubated at 30° C. After 24 days the amount of nitrogen gas in the bottles and the amount of ammonium-nitrogen in the samples were determined. The results are tabulated in Table 8.

(3) The results in Table 8 show that the atmosphere of sample B to which was added ammonium sulfate, contained 4.5 mg more nitrogen gas than that of the check sample A. A comparison of the ammonium-nitrogen content of the fertilized sample B before and after the experiment showed a decrease of 5.66 mg. These results strongly indicated that nitrogen gas is produced in flooded paddy soils from ammonium-nitrogen as a result of denitrification.

B. Effects of Concentrated nitrogenous fertilizers and influence of their application methods on rice yields 19/

1. The customary fertilizer practice employed by the average Japanese farmer for rice production has been to apply commercial fertilizers after flooding the field with irrigation water. By such a method of application, however, the water soluble fertilizers, such as ammonium sulfate, and sometimes even organic fertilizers, if they are in the powdered form, can not be mixed well with the soil of the lower parts of the furrow slice by the usual methods of harrowing. The result is that a considerable amount of the nitrogen applied in the basic application is lost under flooded conditions, probably through denitrification process, the effects of such water-soluble nitrogenous fertilizers as ammonium sulfate are determined largely by the method of application.

2. In order to determine the effect of the time of application on rice yield, the following field experiment was conducted at the Agricultural Experiment Station, Konosu, Saitama Prefecture, in the spring of 1941. Four small adjacent plots were selected and each was divided into three equal lots of 9.43 square meters in area. Ammonium sulfate was applied once to each lot at one of the following stages during the preparation of the rice fields: (1) Two days before flooding; (2) before second harrowing; (3) before third harrowing. Ammonium sulfate was applied broadcast at the rate of 47 Kg of nitrogen per hectare and was worked into the soil of the furrow slice by harrowing with a hoe. Superphosphate and potassium sulfate were applied immediately before the third harrowing at the rates of 75 Kg of P_2O_5 and 75 Kg of K_2O per hectare, respectively.

3. The results of this experiment showed that application of ammonium sulfate before flooding resulted in higher yield of rice than when it was applied at any time after flooding (Table 9). During the course of the experiment the distribution of ammonium-nitrogen in the furrow slice was determined immediately before the second harrowing, before the third harrowing, and after transplanting. Analysis at these periods show that the ammonium-nitrogen was distributed deeper in the furrow slice when ammonium sulfate was applied before flooding then after flooding (Table 10). A comparison of the data in Tables 9 and 10 shows that deep distribution of ammonium-nitrogen results in higher yields of rice.