was obtained from this portion. Its picrate forms yellow prisms, melted at 202°C (uncorr.). The chloroplatinate forms yellow thin plates, easily soluble in water, decomposed at 226°C (uncorr.).

0.0241 g. Subst.	0.0086 g. Pt	35.68% Pt
Calc. for Ornithinechloroplatinate ($C_6H_{12}N_2O_2 \cdot 2HCl \cdot PtCl_4$)		35.95% Pt

Summary.

The yield of the nitrogenous compounds, isolated from 8 litres of rice-vinegar, is as follows.

Adenine (as hydrochloride)	0.40 g.	Putrescine (as hydrochloride)	2.20 g.
Ornithine (")	0.10 g.	Ammonia	2.19 g.

On the Changes of Cyanamide in the Soil. II.

The Decomposition of Dicyanodiamide and Guanylurea in Paddy-soil.

By

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I. Introduction.

A previous investigation by the author (Nippon Nogeikwagaku Kwaishi and this Bulletin, 1930) showed that the formation of ammonia from cyanamide, mainly through urea, is almost same under both soil conditions, namely dry-field (normal soil) and paddy-field (water-logged soil). However, there is a noted difference in the water-logged soil when dicyanodiamide is transformed from cyanamide. Under the water-logged soil condition dicyanodiamide is comparatively easily ammonified, especially in the summer when the soil temperature is relatively high. The author has proved that this is the main reason for the special fertilizing value of dicyanodiamide upon the paddy-rice, in contrast to its harmful effect on ordinary farm crops.

Further studies on the decomposition of dicyanodiamide and its related compound, guanylurea, in water-logged soil have been carried out by the author, with the object of solving some of the problems regarding the unusual decomposition of nitrogenous compounds in paddy-soil.

II. Influence of soil types, temperature, and soil treatment upon dicyanodiamide-decomposition in water-logged soil (with 5 tables in original paper).

1. 7 different soil samples from paddy-fields and dry-fields were tested under the water-logged condition, at the incubation temperature of $30\sim 36^{\circ}\text{C}$; the ammonification of dicyanodiamide in above condition is a general phenomenon, influence of different soil types upon the dicyanodiamide decomposition is not distinct, but rather complicated, and largely depends on the soil treatment.

2. The optimum temperature for the ammonification of dicyanodiamide in water-logged soil is $35\sim 45^{\circ}\text{C}$. In Kagoshima section, during July and August, the temperature above 30°C prevail in the surface water and the soil surface of paddy-fields, and on cloudless days the temperature of the surface water occasionally reaches 40°C , hence the temperature that may be regarded as favorable for dicyanodiamide decomposition seems to be frequently attained in the paddy-soil during paddy-rice cultivation.

3. Air drying of the soil, whether exposed to direct sunlight under natural conditions, or in the diffused light of the laboratory, markedly increases the ammonifying power of the soil in a water-logged state, both for the soil organic nitrogen and the added dicyanodiamide. For example, the rate of ammonia-formation from dicyanodiamide in the water-logged condition by an air-dried soil was two times more than that by the fresh soil, being 10 mg. nitrogen per 100 g. dry soil in the former case against 4 mg. nitrogen in the latter, at the end of 6 weeks with an incubation temperature of $30\sim 36^{\circ}\text{C}$. The emission of a putrid smell always took place when the air-dried soils were incubated in a water-logged condition.

4. A preparatory treatment of the soil with toluene or ether, or the addition of 0.25% mercuric chloride to the water-logged soil, nearly stops the ammonification of dicyanodiamide in the water-logged condition, at $25\sim 28^{\circ}\text{C}$. The presence of 0.125% mercuric chloride in the water-logged soil, however, does not completely suppresses this action at the same temperature.

III. Mechanism of the decomposition of dicyanodiamide (with 10 tables).

1. The formation of guanylurea from dicyanodiamide was noticed when the soil was partially sterilized. From this fact it seems that, in the course of the ammonification of dicyanodiamide, at least some portion of the dicyanodiamide would be converted to guanylurea as an intermediate product. The conversion of dicyanodiamide to guanylurea is probably brought about by a purely chemical (or physico-chemical) process, such as hydrolysis, but not by living micro-organisms, while the formation of ammonia from guanylurea in water-logged soil may be due to the agency of active micro-organisms. Whether, however, the intermediate production of guanylurea from dicyano-

diamide by nonmicrobial agency is the decisive factor for the ammonification of dicyanodiamide in water-logged soil, or the direct ammonification of dicyanodiamide by microbial activity is the main process of dicyanodiamide-decomposition, is not yet clear. The affirmation of this question needs further investigation.

2. Guanylurea is well absorbed by the soil, but the large parts of guanylurea in the soil are leached by the author's method of soil extraction, the method being the treatment of the soil with ferric sulphate solution and lime powder previous to the filtration.

3. The separate determination of dicyanodiamide and guanylurea in the soil may be accomplished by the treatment of the soil sample with copper sulphate solution etc., as dicyanodiamide alone appears in the filtrate, and guanylurea remains in the soil residue.

4. A marked difference in the rate of ammonification of guanylurea between normal soil and water-logged soil is noted, as in the case of dicyanodiamide. Guanylurea, examined in the forms of sulphate and phosphate, is very slowly ammonified in the normal soil condition, as already pointed out by Jacob and others (J. Agr. Res., 1924.), while it is relatively rapidly decomposed in water-logged soil, its ammonification being more rapid than that of dicyanodiamide.

5. It is of interest to find the variation of dicyanodiamide decomposing power by the same paddy-field soil in different season of the year. The soil, which was taken in February from a paddy-field under fallowing in the normal soil condition, ammonified only 5 mg. of dicyanodiamide nitrogen per 100 g. dry soil within 30 days at incubation temperature of 26~28°C when it was brought to the water-logged condition immediately after it was taken from the field, while, in September, when the field was in the later stage of paddy-rice cultivation (It was maintained in a flooded condition for nearly 3 months) the same soil ammonified 8.5 mg. of dicyanodiamide nitrogen per 100 g. of dry soil within 21 days at the same incubation temperature. This difference in the dicyanodiamide-decomposing power may be more largely due to the effect of the soil aeration or the water-logging to which the paddy-field was subjected and less to the mere seasonal difference. The "Kan-den", that is the paddy-field having good drainage, is usually flooded only during the season of paddy-rice cultivation (that is, from early summer to autumn), and after that time (from fall to spring), the field is in the normal soil condition. In the laboratory trials, similar results were obtained with regard to the influence of soil aeration and water-logging upon the dicyanodiamide-decomposing power of a soil. A soil kept in normal soil condition for a month has shown a strong retarding tendency for the dicyanodiamide-decomposition

in the water-logged condition. The longer the period during which the soil was subjected to water-logging, the more the dicyanodiamide-decomposing power was increased.

6. The relations of soil cultivation system and soil treatment to the ammonification of guanylurea in water-logged soil are quite identical to that of dicyanodiamide decomposition. Comparing two soil samples, taken in September from different plots in the same field (the normal soil plot under buckwheat and the paddy-soil plot under paddy-rice), a marked difference was observed in the rate of guanylurea-ammonification in the two soils. With the addition of 10 mg. guanylurea-nitrogen per 100 g. dry soil the rate of ammonification was only 2.6 mg. by the normal soil against 8.3 mg. by the paddy-soil (both in a water-logged condition) after 20 days incubation at $26 \sim 28^{\circ}\text{C}$. A more striking reduction in the guanylurea-ammonifying power in the water-logged condition was observed when the paddy-soil sample was stored under normal soil condition (at a moisture content of one-half saturation) for 2 months, in a wide-mouthed bottle with cotton plug, in the laboratory. The stored samples had a tendency to grow more acid and the pH value decreased from 6.0 to 4.7 after 2 months, when it was brought to a water-logged condition and incubated at $26 \sim 28^{\circ}\text{C}$, it did not show the guanylurea-ammonifying power at all even after 30 days.

From these facts, it may be said that, the prolongation of a liberal aerobic condition in the normal soil state is detrimental to the agency for the guanylurea-ammonification process. On the arable soil of the ordinary farm, however, the soil condition that may be regarded as harmful for the guanylurea-ammonifying agency will not be present over long periods but will be effected by frequent rainfalls and temporary drying of the surface soil, etc.. Consequently, most soils always show, to some degree, the guanylurea-ammonifying power, when the soils are brought to a water-logged condition.

7. The guanylurea-decomposing power of the soil, which was weakened or almost lost by subjecting the soil to aerobic, normal, soil conditions, was gradually restored by the addition of calcium carbonate when the soil was water-soaked, thus increasing the decreased pH value of the soil; where the addition of 0.5 g. calcium carbonate per 100 g. dry soil was made, the pH value of the soil quickly rose from 4.7 to 6.2, and to 7.3 after 30 days incubation. The weakened guanylurea-ammonifying power of the soil was, also, restored without increasing the pH value, but simply inoculating the soil with the paddy-soil (5 g./100 g.), which was kept in the water-logged condition for a long time.

From above results, it can be assumed that the improvement of the guanylurea-ammonifying power of the soil should not be ascribed merely to

the modification of the pH value of the soil, but may be explained by the oxidation-reduction potentials of the soil. Under an environmental condition of a high oxygen tension, where pH is markedly raised, the partial sterilization of soil seems to take place, thus destroying certain species of the guanylurea-ammonifying micro-organisms.

IV. Conclusion.

In the majority of water-logged soils, dicyanodiamide is ammonified at the usual summer temperature.

In the course of the ammonification of dicyanodiamide, at least some portion of dicyanodiamide is converted into guanylurea as an intermediate decomposition product.

The environmental conditions, under which the soil is subjected prior to the incubation of water-logged state, greatly affect the ammonification of dicyanodiamide and guanylurea. In an environment of a high oxygen tension, the partial sterilization of soil seems to take place and destroys certain species of dicyanodiamide and guanylurea-ammonifying micro-organisms.