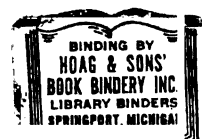


AMMONIUM FIXATION AND AVAILABILITY
IN TAIWAN SOILS

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ABSTRACT

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by Kai-yuan Li

Procedures were proposed for the determination of fixed ammonium and total nitrogen in soils, involving removal of organic and exchangeable nitrogen by calcination and complete release of fixed ammonium in the mineral residue of Kjeldahl digestion by means of concentrated HF. The methods are simple and precise.

The content of natural fixed ammonium in 66 soil profiles in Taiwan was found to range from 1.08 to 2.10 me. per 100 g. soil in the surface soils and from 0.95 to 2.50 me. per 100 g. soil in the subsoils. The ammonium fixing capacity of 12 soil profiles in Taiwan ranged from 1.35 to 2.19 me. per 100 g. soil in the surface soils and from 1.44 to 2.97 me. per 100 g. in the subsoils. The clay minerals of the soils were illite, hydrous mica and vermiculite. The distribution of fixed ammonium in the soil profile was related to the distribution of clay in the soils. The low ammonium fixing capacity of surface soils was probably due to the presence of NH_4^+ and K^+ fixed earlier.

The ammonium fixing capacity of soil with $(\text{NH}_4)_2\text{HPO}_4$, $(\text{NH}_4)_2\text{SO}_4$ and NH_4OH varied between 2.52 and 2.87 me. per 100 g. soil. The results were statistically not significant. Under moist and frozen conditions, the fixation values ranged from 2.51 to 2.59 me. per 100 g. soil.

When the soil was oven-dried, the quantity fixed increased, varying from 2.53 to 2.87 me. per 100 g. soil. The clay minerals of the soil contain vermiculite that was known to fix ammonium under both moist and dry conditions, and that oven-drying would increase fixation even more.

The availability of fixed ammonium in soil during a period of 2 months varied between 2.86 and 25.83 per cent, being lowest for untreated soils and highest for those inoculated with soil extract of Hsi-chu, Hsiaokang Hsiang. When 1.5 me. K was added to the soil, the percentage of ammonium released was markedly decreased. The results showed that K does interfere with the release of fixed NH_4^+ in soils.

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INTRODUCTION

The fixation of ammonia by the mineral fraction of soil has received considerable attention in recent years. Fixed ammonium has been defined as the NH_4^+ in soil or clay minerals that does not exchange with K^+ , although it will exchange with other cations (12, 53). The dominant factor influencing ammonium fixation by 2:1 layer silicate minerals is thought to be the interlayer charge (14). Vermiculite, the hydrous micas, and montmorillonite fix appreciable quantities of NH_4^+ (14, 22, 33, 79) and fixed ammonium occurs in soils containing these minerals (23, 40, 67, 80). Since many soils in Taiwan contain these clay minerals (29, 30, 76, 77), it seems likely that they will also contain fixed ammonium due to reaction of the minerals with ammonium either formed naturally or added in the form of fertilizer. Evidence for the presence of fixed ammonium in Taiwan soil was provided by Wang *et al.* (74, 75), who showed that 11-59 per cent of the total nitrogen in certain sugar cane soils was present in the fixed form. Most of the Taiwan soils have been growing sugar cane or other crops for many decades and some have received in the course of time considerable dressings of ammonium fertilizer. The fixation of ammonium by soils has not been extensively studied, especially in Taiwan. With rapid increase in the use of ammonium fertilizers, more information about ammonium fixation and release is needed particularly in respect to methods of studying this fixation and the difficulties involved.

The objectives of this study are (a) to study and develop the methods of determining fixed ammonium as well as total nitrogen, (b) to study the problem of NH_4^+ -fixation of the soils in some Taiwan soil profiles, (c) to study the effect of K^+ as well as other factors on the availability of fixed NH_4^+ in some Taiwan soils.

REVIEW OF LITERATURE

Ammonium fixation by soil was first recognized by McBeth (49) in 1917, who reported that no more than 81 per cent of the NH_4^+ ions added to a California soil could be recovered after prolonged extraction with 10 per cent hydrochloric acid. He also concluded that various anions did not affect fixation, that fixation was greater at 100° C than at 5° C, and that ammonium retention took place in the clay fraction. Olsen (57) employed a HCl-KCl extractant, a solution that would extract some of the non-exchangeable as well as the exchangeable ammonium from soils. Gedroyts (34) made a distinction between intensely exchangeable cations and not readily exchangeable cations, the majority of which could not be removed from the soil by the usual methods of extracting adsorbed cations. Chaminade and Drouneau (26, 27) presented evidence that non-exchangeable ammonium accumulated in some French soils which had received several applications of ammonium fertilizer over a period of years. They found that this cation fixed by the clay fraction of soils could be liberated by ball-milling or treatment with hydrofluoric acid.

According to Barshad (14), only three-layer clay minerals with expanding lattice possess the capacity to fix NH_4^+ and K^+ . The magnitude of this capacity depends on the total interlayer charge. Minerals with interlayer charge of 210 me. per 100 g. and more have the greatest fixation capacity (160-200 me. per 100 g.). It is lower in

minerals with a charge of 150-160 me. per 100 g., amounting to about 50% of the total adsorption capacity. Minerals with an interlayer charge of less than 106 me. per 100 g. are not able to fix NH_4^+ and K^+ whatsoever. Therefore, vermiculite and muscovite that have an interlayer charge of 262 and 216-219 me. per 100 g., respectively, have the highest fixation capacity (200 me. per 100 g.). Montmorillonite, having a charge of 110-115 me. per 100 g., has a much lower fixation capacity (2-2.5 me. per 100 g.).

According to the data of various investigators, the content of fixed ammonium in the majority of soils amounted to 0.3 to 3.5 me. per 100 g. in the upper horizons and 0.4 to 5.0 me. per 100 g. in the lower (35, 60, 69). In the opinion of Allison et al., the fixing capacity of the subsoil was greater than that of the corresponding surface soil, because the fixing capacity of the surface soil had been somewhat saturated with fixable potassium and ammonium ions applied in fertilizers, released from weathering of primary minerals, and formed during the decomposition of organic matter.

Gruner (36) was able to form an ammonium-mica from vermiculite by treatment with NH_4OH and drying at 50°C . Fixation of NH_4^+ by bentonite upon drying was observed by Page and Baver (58) and Joffe and Levine (44). Bower's (19) finding that the exchangeable Na content of some California soils sometimes exceeded the cation exchange capacity as determined by adsorption of NH_4^+ led to the discovery of moist NH_4^+ -fixation. He had shown that under moist conditions some soils of semiarid regions were capable of fixing relatively large amounts of applied NH_4^+ as well as K^+ in difficultly exchangeable form.

Allison et al. (1, 3) and Legg et al. (46) reported that removal of water from the soil after the addition of ammonium would considerably increase the fixation capacity of moist soils. The moist fixation values were increased two or three times by air-drying and oven-drying increased fixation even more. For instance, Allison et al. (1) found that the Ap horizon of a Harpster clay loam was able to fix 1.1, 3.5, and 6.2 me. NH_4^+ per 100 g. soil under moist, air-dried, and oven-dried conditions, respectively. Barshad (10) showed that vermiculite, when repeatedly heated (20 to 30 times) to 70° C. for several hours with fresh 1 N ammonium solutions, fixed large quantities of ammonium in a form not readily or completely replaced by K^+ , Rb^+ , or Cs^{++} ions, but removed by Li^+ , Na^+ , Mg^{++} , Ca^{++} , and Ba^{++} . Allison et al. (4) having worked with samples of vermiculite, reported fixation values of approximately 40 and 80 me. per 100 g. when unheated, and 45 and 85 me. when heated at 100° C for 24 hours. Young et al. (79) reported that vermiculite minerals under wet or air-dry conditions fixed quantities of NH_4^+ greatly in excess of the amounts fixed by other minerals. The effect of temperature on the sorption of ammonia by calcium bentonite was studied by Mortland (51). The amount of ammonia sorbed decreased with increasing temperature. Walsh and Murdock (70) found that an additional 5% of the added NH_4^+ was fixed in each horizon when the soil was frozen after applying NH_4^+ . Very little information concerning the effect of freezing on ammonium fixation was found in the literature.

Sorption isotherms of ammonia on base-saturated clays had been utilized by Mortland (51, 53), Zettlemeyer et al. (81) and Mortland and Erickson (55) for the determination of specific surface. In the case

of nitrogen, small specific surface figures were obtained for montmorillonite, indicating that the nitrogen was not penetrating the interlayer surface. Upon use of ammonia, large specific surface figures were obtained indicating that this highly polar molecule was capable of penetrating the interlayer surfaces of montmorillonite.

The carbon-nitrogen ratio of the soil generally decreased with increasing depth in the soil profile. Hardy and Rodrigues (39) demonstrated the accumulation of large amounts of ammonium in simple exchangeable form in certain sugar cane soils of British Guiana. These accumulations were first revealed by the extremely low values obtained for carbon-nitrogen ratio in the lower horizons of certain soil profiles. Narrowing of the carbon-nitrogen ratio with depth appeared to be due in part to fixed ammonium (60, 66, 67, 74, 75).

In the opinion of some investigators, not only clay minerals, but also the organic substances of the soil had the ability to fix ammonium in a nonexchangeable form. Mattson and Anderson (48) considered that a chemical reaction involving simultaneous oxidation and ammoniation was responsible for the increase in stable organic nitrogen which they found in peat and humus materials after aerating them in the presence of NH_4OH . On the basis of their work with humus materials and polyphenolic compounds they theorized that fixation took place in the lignin fraction of soil organic matter and required the presence of an aromatic possessing more than one hydroxyl group. Bennet (15) reported that aerobic ammoniation of a commercial lignin reduced its capacity to form methoxyl groups upon treatment with methyl sulfate. Conversely, methylation reduced the amount of ammonia that could be

fixed. Burge and Broadbent (25) had verified the capacity of the organic substance of soil to fix ammonium in the nonexchangeable form. They showed experimentally that the major role in fixation was played by the hydroxyl groups of organic substances. Sohn and Peech (63) measured the ammonia-fixing capacity of a number of soils when treated aerobically with anhydrous ammonia. They concluded that at least half of the ammonia fixed must be attributed to fixation by the organic fraction.

According to Ayres (9), NH_4^+ and K^+ ions were taken up in different ratios when the concentrations of these cations were varied. Thus, at high concentrations, more NH_4^+ than K^+ ions were absorbed by the soils. With decreasing concentrations, however, relatively more K^+ ions were absorbed, until at a concentration of 0.1 N, the NH_4^+ ions taken up were slightly in excess of the K^+ ions. Fixation of K^+ or NH_4^+ had a depressive effect on the subsequent fixation of the other, both for bentonite (45) and for vermiculite (10). Stanford and Pierre (65), however, reported a close correlation between the K^+ - and NH_4^+ -fixing capacity of Webster silty clay loam when these ions were supplied in equivalent amounts. They also proved that prior fixation of ammonium or potassium caused an equivalent reduction in the subsequent fixation of the other ion. On the basis of these results, it was concluded that the two ions are fixed by the same mechanism. Peech (59) emphasized an effect in soils which could be explained by the same mechanism, namely, the pronounced blocking effect of ammonium ions on the release of nonexchangeable K^+ . The choice of ammonium acetate as an extractant of exchangeable cations was adduced for a separation of exchangeable from non-exchangeable K^+ .

Nitrification studies indicate that very little fixed NH_4^+ was nitrified even during prolonged incubation periods, whereas exchangeable NH_4^+ was readily nitrified (3, 6, 7, 20). Allison et al. (2) found that 7% of the applied NH_4^+ fixed by soil was available to millet when fixation had been brought about by air drying and 12% when by oven drying at 100° C. In another experiment Allison et al. (1) reported that only 10% of the applied NH_4^+ fixed in a Harpster clay loam was available to nitrifying bacteria. Bower (20) showed that only 13 to 28% of the difficultly exchangeable ammonium in semiarid soils was available to nitrifying bacteria. In modified Neubauer experiments, 10% of the fixed ammonium was assimilated by barley plants. These findings led Bower to conclude that bacteria could more effectively remove applied NH_4^+ fixed by soils than could higher plants.

Nommik (56) and Jansson (43) studied the effect of added K^+ on the availability of NH_4^+ added to an NH_4^+ -fixing soil. When K^+ was added simultaneously with NH_4^+ , instead of NH_4^+ alone, there was less carbon mineralization by heterotrophic microorganisms and less nitrogen uptake by plants. Welch et al. (72) found that nearly all the NH_4^+ fixed by three different vermiculites was nitrified in the absence of added K^+ , but at moderate to high levels of K^+ virtually none of the applied NH_4^+ fixed by the clay minerals was nitrified. Mortland et al. (52) showed that fixed K^+ was removed from vermiculite by four successive crops of wheat. X-ray diffraction patterns showed a loss of the 10 Å. peak and reappearance of the 14 Å. peak after cropping. This indicated that vermiculite which had collapsed on K^+ saturation was expanded to its normal spacing when the K^+ was removed by the crop.

MATERIALS AND METHODS

The soils which formed the basis of this study were selected from the important sugar cane fields of Taiwan that had been intensively cultivated under the crop rotation system, a legume-plant sugar cane-first ratoon cane.

The following soils were used:

Soil no.*	Soil varieties	Localities
1 - 3	Lateritic soils	Shan-tzu-chiao, Taichung
4 - 6	"	Heng-shan, Taichung
7 - 8	"	Chih-shan, Pingtung
9 - 11	Slate alluvial soils	Erh-lin, Chihu
12 - 14	"	Erh-lin, Chihu
15 - 17	"	Yung-an, Chihu
18 - 20	"	Yung-an, Chihu
21 - 23	"	Chung-hsi, Chihu
24 - 26	"	Hsin-tso, Pingtung
27 - 28	"	Hsin-tso, Pingtung
29 - 31	"	Wan-tan, Pingtung
32 - 34	"	Hou-pu, Nanchou
35 - 37	"	Hou-pu, Nanchou
38 - 40	"	Hou-pi-tso, Nanchou
41 - 42	"	Hou-pi-tso, Nanchou
43 - 45	Clay-sandstone alluvial soils	Tiao-chi-lin, Chiaotou
46 - 48	"	Chung-tzu-lin, Chiaotou

Soil no.*	Soil varieties	Localities
49 - 51	Coral-limestone alluvial soils	Chiu-kuei, Chiaotou
52 - 54	"	Chiu-kuei, Chiaotou
55 - 57	"	Chung-chu, Hsiaokang
58 - 60	"	Chung-chu, Hsiaokang
61 - 63	"	Nan-chu, Hsiaokang
64 - 66	"	Nan-chu, Hsiaokang

*Each soil number refers to a single soil layer. The span of numbers for each location indicates the number of layers for that particular site.

Soils used for studying total nitrogen and fixed ammonium were samples no. 1 to 66. Sample no. 45 (Tiao-chi-lin, Chiaotou) known to possess high ammonium fixation capacity was used for studying the fixation of ammonium of different carriers, as well as under moist, frozen and oven-dried conditions, and the release of fixed ammonium as affected by potassium addition. Before use the soils were air-dried and ground to pass a 2 mm. (9 mesh) sieve.

Three minerals, Illinois illite, Wyoming bentonite and Montana vermiculite obtained from Ward's Natural Science Establishment, Inc. were used in this work.

The chemicals used were analytical grade products obtained from J. T. Baker Chemical Co., and Wako Pure Chemical Industries, Ltd.

Unless otherwise stated, nitrogen was determined by the Bremner's modified Kjeldahl method (24) and that modified by the author. Fixed ammonium of all soils was determined by Mogilevkina's method (50) and the author's proposed method. Fixed ammonium of the digested soil was determined by Stevenson's method (67) and the HF method.

The quantity of ammonium ion fixed was determined according to Allison et al. (1). The removal of exchangeable potassium of the calcined soil for nitrification test was conducted according to the procedure described by Allison et al. (1, 2). Soil of Hsi-chu, Hsiaokang Hsiang known to contain active nitrifying flora (78) was used for the inoculant.

pH was measured with a Beckman Zeromatic pH meter. Mechanical analysis of soils was made by Bouyoucos hydrometer method (17, 18). Organic matter of soils was determined by Walkley-Black method (68). Exchangeable potassium of soils obtained in the NH_4OAc extraction was determined by means of the cobaltinitrite procedure (42). The mineral fractions of the samples were analyzed for types of clay minerals by X-ray diffraction after digestion of the organic matter with acidified H_2O_2 , as described by Jackson (42). X-ray diffraction patterns were obtained with a Norelco unit employing $\text{CuK}\alpha$ radiation, Geiger-Mueller tube, and a Brown recorder.

Blank controls were included in each set of determinations.

RESULTS AND DISCUSSION

I. Study on the methods of fixed ammonium determination

1. Rise of the problem

Barshad (12) proposed an alkali distillation method, based on the fact that fixed ammonium was extracted from soils and clay minerals during their distillation with NaOH and not with KOH (10). Fixed ammonium was determined from the difference between the amounts of ammonium extracted with 0.2 N NaOH and 0.2 N KOH. It was assumed that distillation of soil with NaOH and KOH released equal amounts of ammonium as a result of the deamination of organic nitrogen compounds. According to Hanway (37), distillation with NaOH (Barshad's method) was not always effective. Studies showed that the results could be different, depending on the duration and intensity of distillation. It was also found that NaOH did not extract all of the fixed ammonium. The presence of a small amount of K^+ in the soil reduced the ability of NaOH to displace fixed ammonium considerably. To remove exchangeable potassium, it was suggested that the soil be first treated with N NaCl. But in this case also complete extraction of fixed ammonium was not achieved and the results obtained were much too low (22, 23).

Rodrigues (60) suggested a method which involved the extraction of fixed ammonium from the soil with hydrofluoric acid, which was capable of decomposing clay minerals. The soil was treated with a 4:1 mixture of 40% HF and 50% H_2SO_4 for one hour and the ammonium determined

in the extract by distillation with alkali. But the investigations showed that when such mixed acids and especially subsequent distillation with alkali were used for extraction, a considerable amount of ammonia had formed as a result of the decomposition and deamination of organic nitrogen compounds (amides and hexoseamines).

In Bremner's method (22) fixed ammonium was extracted with a solution of HF and $\underline{N}$ HCl for 24 hours and at last with $\underline{N}$ KCl. The amount of ammonium removed in the extract was determined by means of slow distillation with a borate buffer solution (pH 8.8). But the investigations also showed that a considerable amount of ammonium had formed as a result of the decomposition and deamination of organic compounds. Schachtschabel (61) indicated that extraction of ammonium fixed by the soil by diluted HF solutions in a short period (Rodrigues' and Bremner's methods) was incomplete.

Dhariwal and Stevenson (32) used strong KOH solution to decompose the organic nitrogen and to drive off the ammonium ion and subsequently a mixture of $5 \underline{N}$ HF + $\underline{N}$ HCl + $0.6 \underline{N}$ H₂SO₄ to extract fixed ammonium from the soil. They determined the ammonium removed in the extract by means of slow distillation with MgO, using the microdiffusion method of Conway (31), modified by Bremner and Shaw (21). Schachtschabel (61) showed however that these operations were not effective enough and the organic matter could not be completely removed by autoclaving together with strong KOH solution.

Scott, Edwards and Bremner (62) have tried to use cation-exchange resins to extract fixed ammonium from clay minerals saturated with fixed ammonium, and found it little effective.

In Schachtschabel's (61) method, fixed ammonium was extracted with concentrated H_2SO_4 and 40% HF on a sand bath after the organic substance had been destroyed by hydrogen peroxide in presence of KCl. After vigorous reaction, two portions of 40% HF were added to the soil to increase the effect of HF. But work with HF on a sand bath was inconvenient because of its volatility, and required special precautions. Owing to the fact that HF itself contained some ammonium, the amount used must be accurately measured, and the result obtained must be accordingly corrected. The use of HF requires plastic containers, measuring vessels, etc.

Mogilevkina (50) proposed a soil calcination method, according to which the portions of the organic matter including amide and hexoseamine N and the exchangeable ammonium were burned from the soil at 450°C and the fixed ammonium was released by means of H_2SO_4 digestion and determined according to Bremner's method (24).

2. Method and result of the investigation of Mogilevkina's method

It can be seen from the foregoing paragraphs that most of the methods are entangling with incomplete separation of the organic nitrogen and the exchangeable ammonium from the ammonium fixed in the crystal lattice of the soil clay minerals. Mogilevkina's method seems promising. The following investigations were conducted to check its soundness. Mogilevkina (50) found 450°C was the optimum calcination temperature for hydrobiotite. Whether this temperature was also optimum for bentonite, illite, vermiculite, etc. remained to be confirmed.

Calcination test:

Chaminade (28) calcined minerals containing absorbed ammonium in exchangeable and fixed form and found that fixed ammonium could be completely removed by heating to 500° C. Bottini (16) heated ammonium permutite, ammonium bentonite, and ammonium clay at 50 to 550° C and also showed that strongly bound ammonium was removed at temperature from 500 to 550° C. At the same time, separation of exchangeable ammonium began at 50° C and apparently ceased at 350 to 450° C. Mogilevkina (50) treated a mixture of soil and hydrobiotite with a known content of fixed ammonium at 400° C and found that calcination at 400° C could be used as an effective means of removing organic matter and exchangeable ammonium from the soil, while the fixed ammonium remained intact.

Accordingly, three minerals, Illinois illite, Wyoming bentonite and Montana vermiculite obtained from Ward's Natural Science Establishment, Inc. were used as the materials to be tested. Bulk samples of the air-dried minerals were ground to pass a 0.33 mm. (40 mesh) sieve. The procedure of the calcination test was as follows: 40 g. of each of the mineral samples was placed in a 500 ml. Erlenmeyer flask and saturated with $\text{N (NH}_4\text{)}_2\text{SO}_4$ solution. The samples were heated at 110° C for 24 hours according to the procedure described by Allison et al. (1). The excessive ammonium salt and exchangeable ammonium of each of 100 g. sample were removed by leaching with 800 ml. N KCl solution and 1000 ml. water until the leachate became negative to the Nessler's reagent. Before use the samples were dried in an oven at 50° C (42). Then 2 g. each, was placed in a porcelain dish (55 mm.

diam., 10 mm. ht.) and heated in a muffle furnace at 300, 350, 400, 450, 500 and 550° C, separately, for 36-40 hours. The total N of the original clay minerals, the fixed ammonium of the clay minerals, having been leached with N KCl solution and those of the thermal calcined clay minerals were analyzed by the author's proposed method to be described later (see page 18). Table I shows the amount of ammonium in the three clay minerals after the different treatments.

Table I. Amounts of ammonium after calcination in illite, bentonite and vermiculite (me./100g) *

Treatments	Illite	Bentonite	Vermiculite
Original minerals	0.27	0.08	0.82
Minerals saturated with <u>N</u> (NH ₄) ₂ SO ₄ , heated to 110° C, for 24 hrs, then leached with <u>N</u> KCl	8.39	1.38	10.26
Minerals saturated with <u>N</u> (NH ₄) ₂ SO ₄ , heated to 110° C, for 24 hrs, then calcined 2 days at			
300° C	11.58	3.02	15.34
350	10.25	2.62	13.11
400	8.43	1.40	10.41
450	8.35	1.35	10.37
500	0.12	0.06	1.59
550	0.00	0.02	0.04

*Data were average of 3 replications.

This experiment showed that calcination in the temperature interval, 300 to 350° C., still retained ammonium and did not affect the content of fixed ammonium. Calcination at the temperature range, 400 to 450° C resulted in approximately the same values of fixed NH_4^+ as those leached with N KCl solution, showing no appreciable loss of fixed ammonium from the three minerals. As the calcination temperature was increased to 500 and 550° C, the loss of fixed ammonium in the three minerals approached completion.

Thus, these data support the assumption made previously that calcination of ammonium-fixing clay minerals at 400° C removed the exchangeable ammonium ion, but not the fixed ammonium.

Digestion of the calcined clay minerals:

Mogilevkina (50) determined the fixed ammonium contained in the clay mineral after calcination by means of Bremner's method of total nitrogen determination. According to the author's experimental results, the Bremner's total nitrogen was always lower than the sum of organic nitrogen, exchangeable ammonium nitrogen and the fixed ammonium nitrogen, as determined by the HF method. With this in view, the following investigation was conducted with the aim of finding the difficulty associated with Bremner's method.

The author tried to examine whether there was still some fixed NH_4^+ remaining in the soil residue left after calcination at 450° C and digestion in concentrated H_2SO_4 according to Mogilevkina's modification of Bremner's method.

Each 2 g. of the residue was digested in a 100 ml. polyethylene beaker with 15 ml. of 5N HF - N HCl - 0.6N H_2SO_4 (67) and another with

6 ml. of cold 40% HF for 16-20 hours occasionally stirring with a polyethylene rod. The sample was then transferred to the distillation unit. Then 20 ml. of NaOH was added to the slurry and the ammonia distilled into 0.0204 N H₂SO₄. The time of distillation was 20 minutes. The amount of ammonia was determined by back titration with 0.0148 N NaOH.

The results, given in Table II, showed that digested residues by Bremner's method as modified by Mogilevkina still contained 0.04 to 0.27 or 0.04 to 0.30 me. per 100 g. soil of fixed ammonium which could be extracted with 5N HF - N HCl - 0.6N H₂SO₄ (67) or 40% HF, respectively. A statistical analysis of the data showed that in only 14 of 66 cases were there significant differences between these two methods of analysis, as reflected by the two series of figures shown.

3. A proposed method of determination of fixed ammonium

Organic matter and exchangeable ammonium were removed by calcination of soil at 400° C for 36-40 hours by the method of Mogilevkina (50). The fixed ammonium contained in the mineral part of the soil was first released by Kjeldahl digestion and then with 40% HF digestion.

The procedure is as follows: 2 g. of soil was placed in a porcelain dish (55 mm. diam., 10 mm. ht.) and heated in a muffle furnace at 400° C (within $\pm 20^\circ$ C) for 36-40 hours. Then the calcined sample was carefully transferred into a 150 ml. Kjeldahl flask. Then 2.5 g. of K₂SO₄, 3.9 g. of CuSO₄·5H₂O, 0.025 g. of Se and 8 ml. of concentrated H₂SO₄ were added into the Kjeldahl flask and the whole was digested for 5 hours. The digested sample was washed with 50-60 ml. of distilled water into polyethylene beaker. The supernatant

Table II. Comparison of method of determining fixed ammonium (me./100g. soil)†

Soil no.	Depth (cm.)	Mogilevkina's method (Bremner)	<u>Ammonium extracted from soil residue after calcination and digestion</u>			Differences	Author's method	Difference between results of Mogilevkina's method & author's method
			5N HF-N HCl-0.6N H ₂ SO ₄	40% HF				
<u>Lateritic soils</u>								
Shan-tzu-chiao, Taichung								
1	0- 30	1.16	0.13	0.12	0.01	1.26	0.10	
2	30- 50	1.26	0.12	0.13	0.01	1.38	0.12	
3	50-100	1.23	0.14	0.14	0.00	1.34	0.11	
Heng-shan, Taichung								
4	0- 30	1.19	0.16	0.15	0.01	1.27	0.08	
5	30- 60	0.94	0.15	0.17	0.02	1.11	0.17*	
6	60-100	1.82	0.18	0.16	0.02	1.83	0.01	
Chih-shan, Pingtung								
7	0- 35	1.12	0.06	0.08	0.02	1.16	0.04	
8	35- 70	1.19	0.04	0.06	0.02	1.21	0.02	
<u>Slate alluvial soils</u>								
Erh-lin, Chihu								
9	0- 30	1.90	0.20	0.20	0.00	2.06	0.16*	
10	30- 70	1.99	0.19	0.17	0.02	2.16	0.17*	
11	70-100	2.17	0.25	0.28	0.03	2.44	0.27*	
12	0- 10	1.14	0.06	0.08	0.02	1.17	0.03	
13	10- 60	1.06	0.04	0.06	0.02	1.11	0.05	
14	60-100	1.24	0.04	0.04	0.00	1.29	0.05	

Table II--Continued

Soil no.	Depth (cm.)	Mogilevkina's method (Bremner)	Ammonium extracted from soil residue after calcination and digestion			Differ-ences	Author's method	Difference between results of Mogilevkina's method & author's method
			5N HF-N HCl-0.6N H ₂ SO ₄	40% HF				
Slate alluvial soils								
Yung-an, Chihu								
15	0- 40	1.61	0.11	0.13	0.02	1.59	0.02	
16	40- 90	1.38	0.16	0.18	0.02	1.46	0.08	
17	90-100	1.72	0.14	0.13	0.01	1.79	0.07	
18	0- 30	1.04	0.04	0.06	0.02	1.09	0.05	
19	30- 80	1.59	0.15	0.14	0.01	1.56	0.03	
20	80-100	1.51	0.12	0.14	0.02	1.57	0.06	
Chung-hsi, Chihu								
21	0- 30	1.13	0.10	0.11	0.01	1.15	0.02	
22	30- 60	1.69	0.19	0.21	0.02	1.74	0.05	
23	60-100	1.41	0.13	0.12	0.01	1.44	0.03	
Hsin-two, Pingtung								
24	0- 35	1.08	0.06	0.07	0.01	1.11	0.03	
25	35- 75	1.39	0.04	0.06	0.02	1.53	0.14*	
26	75-100	1.51	0.08	0.06	0.02	1.57	0.06	
27	0- 40	1.02	0.09	0.09	0.00	1.08	0.06	
28	40-100	1.86	0.12	0.15	0.03	1.95	0.09	
Wan-tan, Pingtung								
29	0- 15	1.52	0.14	0.14	0.00	1.57	0.05	
30	15- 45	1.55	0.12	0.16	0.02	1.60	0.05	
31	45- 80	1.59	0.08	0.09	0.01	1.65	0.06	

Table II--Continued

Soil no.	Depth (cm.)	Mogilevkina's method (Bremner)	<u>Ammonium extracted from soil residue after calcination and digestion</u>			Differ-ences	Author's method	Difference between results of Mogilevkina's method & author's method
			5N HF-	40% HF				
			<u>N</u> HCl- 0.6 <u>N</u> H ₂ SO ₄					
<u>Slate alluvial soils</u>								
Hou-pu, Nanchou								
32	0- 20	1.45	0.12	0.11	0.01	1.51	0.06	
33	20- 55	1.54	0.16	0.17	0.01	1.60	0.06	
34	55-100	1.76	0.10	0.11	0.01	1.70	0.06	
35	0- 45	1.97	0.18	0.19	0.01	2.03	0.06	
36	45- 60	0.86	0.08	0.10	0.02	0.95	0.09	
37	60-100	1.06	0.06	0.06	0.00	1.11	0.05	
Hou-pi-tso, Nanchou								
38	0- 20	1.20	0.22	0.24	0.02	1.48	0.28*	
39	20- 60	1.12	0.16	0.19	0.03	1.51	0.39*	
40	60-100	1.15	0.13	0.09	0.06	1.56	0.41*	
41	0- 40	0.96	0.17	0.19	0.02	1.16	0.20*	
42	40- 60	1.58	0.15	0.19	0.04	1.68	0.10	
<u>Clay-sandstone alluvial soils</u>								
Tiao-chi-lin, Chiaotou								
43	0- 30	1.83	0.19	0.19	0.00	1.97	0.14*	
44	30- 65	2.10	0.17	0.19	0.02	2.27	0.17*	
45	65-100	2.29	0.22	0.24	0.02	2.50	0.21*	
Chung-tzu-lin, Chiaotou								
46	0- 30	1.89	0.18	0.16	0.02	1.96	0.07	
47	30- 60	1.94	0.15	0.18	0.03	1.97	0.03	
48	60-100	1.98	0.14	0.15	0.01	2.00	0.02	

Table II--Continued

Soil no.	Depth (cm.)	Mogilevkina's method (Bremner)	<u>Ammonium extracted from soil residue after calcination and digestion</u>				Differ-ences	Author's method	Difference between results of Mogilevkina's method & author's method
			<u>5N HF</u>		40% HF				
			<u>N</u>	<u>HCl-</u>					
			0.6N	H ₂ SO ₄					
<u>Coral limestone alluvial soils</u>									
Chiu-kuei, Chiaotou									
49	0- 35	1.89		0.14	0.16	0.02	1.96	0.07	
50	35- 60	1.94		0.13	0.13	0.00	1.93	0.01	
51	60-100	1.97		0.13	0.14	0.01	2.01	0.04	
52	0- 15	1.95		0.16	0.18	0.02	2.01	0.06	
53	15- 85	2.00		0.14	0.14	0.00	2.03	0.03	
54	85-100	2.04		0.12	0.14	0.02	2.07	0.03	
Chung-chu, Hsiaokang									
55	0- 40	1.59		0.10	0.11	0.01	1.68	0.09	
56	40- 90	1.46		0.13	0.13	0.00	1.57	0.11*	
57	90-100	1.86		0.16	0.19	0.03	2.01	0.15*	
58	0- 40	1.79		0.19	0.21	0.02	1.87	0.08	
59	40- 90	1.16		0.14	0.17	0.03	1.24	0.08	
60	90-100	1.73		0.17	0.13	0.04	1.79	0.06	
Nan-chu, Hsiaokang									
61	0- 30	2.01		0.27	0.30	0.03	2.10	0.09	
62	30- 60	2.04		0.21	0.22	0.01	2.14	0.10	
63	60-100	2.09		0.12	0.16	0.04	2.19	0.10	
64	0- 35	1.97		0.18	0.22	0.04	2.03	0.06	
65	35- 70	1.89		0.16	0.17	0.01	1.94	0.05	
66	70-100	2.15		0.17	0.17	0.00	2.22	0.07	

Data were average of 3 replications.

* Significant at 0.05 level.

solution was decanted and preserved. Then 6 ml. of 40% HF was added to the residue. After 16-20 hours of occasional stirring with a polyethylene rod, the residue and the supernatant solution were transferred to the distillation unit. Then 45 ml. of 10 N NaOH was added to the slurry. The ammonia was distilled into 0.0204 N H₂SO₄ containing 0.8 ml. of 0.1% alizarin red indicator. The time of distillation was 20 minutes. The excess of the sulfuric acid was back titrated with 0.0148 N NaOH.

The above stated method had been applied to samples of pure ammonium sulphate and ammonium chloride as control. The recovery was satisfactory, as shown in Table III.

Table III. Recovery of nitrogen from ammonium sulphate and ammonium chloride by author's method

Ammonium sources	Aliquots no.	Nitrogen in sample	Nitrogen recovered	
		mg.	mg.	%
(NH ₄) ₂ SO ₄	1	0.35	0.3448	98.5
	2	0.69	0.6845	99.2
	3	1.20	1.2036	100.3
	4	2.13	2.1449	100.7
NH ₄ Cl	1	0.42	0.4150	98.8
	2	0.86	0.8480	98.6
	3	1.47	1.4715	100.1
	4	2.78	2.8412	102.2

The results of the author's proposed method were shown in the 7th column of Table II. They are higher than those of Mogilevkina's modification of Bremner method on 62 samples out of the total 66. The

differences between the results of these two methods are significant on 14 soil samples, as marked with asterisks.

Table II also showed the distribution of fixed ammonium in the various soil depths. The content of fixed ammonium was 1.08 to 2.10 me. per 100 g. soil in the surface soils and 0.95 to 2.50 me. per 100 g. soil in the subsoils. Lateritic soils and slate alluvial soils, clay-sandstone alluvial soils and coral limestone alluvial soils differed little in their content of natural fixed ammonium.

The studies of Barshad (10, 11, 13, 14), Allison (2, 4) and others demonstrated that illite, vermiculite, and montmorillonite were the main minerals that fixed ammonium in nonexchangeable form. Stevenson et al. (66) found that a considerable amount of fixed ammonium was also present in sedimentary and igneous rocks. The fixation of ammonium in soils and rocks was achieved by three layer clay minerals with expanding lattice. These minerals were chiefly found in the clay fraction of the soil. For this reason the distribution of fixed ammonium in the soil profile always goes in parallel to the distribution of clay in it.

II. Study on the methods of total nitrogen determination

1. Rise of the problem

A detailed comparative study of various Kjeldahl methods of determining total nitrogen in soils was conducted recently by Bremner (24) who modified the Kjeldahl method by using K_2SO_4 , $CuSO_4$ and Se as catalysts at an $H_2SO_4 : K_2SO_4$ ratio of 3:1. The reliability of this method had been investigated using a range of soils containing from 0.03 to 2.7% nitrogen.

When determining the total nitrogen of soils, Bremner's (24) modification of the Kjeldahl method was used. A soil sample of 8 g. was placed in a 150 ml. Kjeldahl flask. Then 5 g. of K_2SO_4 , 7.8 g. of $CuSO_4 \cdot 5H_2O$, 0.05 g. of Se and 15 ml. of concentrated H_2SO_4 were added to the flask and the whole digested for 5 hours, and then transferred to a Parnas Wagner distillation unit. Then 8 ml. of 10 N NaOH was added to the slurry. The ammonia was distilled into 0.0204 N H_2SO_4 solution, and the excess of acid back titrated with 0.0148 N NaOH solution.

In view of the previous finding that the fixed ammonium could not be completely released from the crystal lattice by means of concentrated H_2SO_4 digestion and of the fact that fixed ammonium has been found not completely unavailable, the fixed ammonium of a soil should be included in the total nitrogen when analyzed.

2. Method and result of the investigation of Kjeldahl's method

An experiment was made to check whether Bremner's modified Kjeldahl method could effect liberation of fixed ammonium from the soils.

The residue of each of 8 g. soil sample from the digestion in concentrated H_2SO_4 according to Bremner's modification of Kjeldahl's method was collected and filtered with Whatman no. 1 filter-paper, washed with 10-20 ml. 2 N H_2SO_4 and then with 40-50 ml. water until free of NH_4^+ , and at last dried in an oven at 50° C (42). Then 2 g. of the residue was digested with 15 ml. of 5 N HF - N HCl - 0.6 N H_2SO_4 (67) in a polyethylene beaker and another with 6 ml. of cold 40% HF

for 16-20 hours with occasional stirring. Then the whole slurry was transferred to the distillation unit, distilled and titrated as before.

The results tabulated in Table IV showed that the residue of 66 soil samples still contained 0.04 to 0.69 and 0.07 to 0.68 me. per 100 g. soil extractable by 5 N HF - N HCl - 0.6 N H₂SO₄ and 40% HF, respectively, the values extractable by 40% HF being generally higher though significantly so in only 21 of 66 cases.

3. A proposed method of determination of total nitrogen

In view of these results the author tried to develop a method of determining total nitrogen by Kjeldahl digestion in conjunction with 40% HF digestion of the residue.

The procedure was as follows: 2 g. of soil was placed in a 150 ml. Kjeldahl flask. Then 2.5 g. of K₂SO₄, 3.9 g. of CuSO₄·5H₂O, 0.025 g. of Se and 8 ml. of concentrated H₂SO₄ were added to the flask and the whole digested for 5 hours. The solution and the residue were transferred into a 100 ml. polyethylene beaker with 50-60 ml. of distilled water. Then, the supernatant solution was decanted and preserved. Then, 6 ml. of 40% HF was added to the residue and digested 16-20 hours with occasional stirring by means of a polyethylene rod. Then the slurry and the supernatant solution previously collected were transferred to the distillation unit. Then 45 ml. of 10 N NaOH was added and the ammonia was distilled into 0.0204 N H₂SO₄ solution containing 0.8 ml. of 0.1% alizarin red indicator during a period of about 20 minutes. The excess of the acid was back titrated with 0.0148 N NaOH solution.

Table IV. Comparison of methods of determining total nitrogen (me./100g. soil)#

Soil no.	Depth (cm.)	Bremner's method (Kjeldahl)	<u>Ammonium extracted from soil residue after calcination and digestion</u>			Differ-ences	Author's method	Difference between results of Bremner's method & author's method
			5N HF- N HCl- 0.6N H ₂ SO ₄	40% HF				
<u>Lateritics soils</u>								
Shan-tzu-chiao, Taichung								
1	0- 30	3.72	0.39	0.39	0.00	4.07	0.35*	
2	30- 50	3.69	0.36	0.39	0.03	3.91	0.22	
3	50-100	3.10	0.22	0.24	0.02	3.13	0.03	
Heng-shan, Taichung								
4	0- 30	4.25	0.26	0.25	0.01	4.55	0.30*	
5	30- 60	4.05	0.23	0.26	0.03	4.32	0.27	
6	60-100	3.56	0.21	0.23	0.02	3.79	0.23	
Chih-shan, Pingtung								
7	0- 35	4.03	0.10	0.11	0.01	4.13	0.10	
8	35- 70	2.90	0.09	0.09	0.00	3.03	0.13	
<u>Slate alluvial soils</u>								
Erh-lin, Chihu								
9	0- 30	6.56	0.34	0.34	0.00	6.94	0.38*	
10	30- 70	5.88	0.31	0.32	0.01	6.09	0.21	
11	70-100	5.09	0.22	0.27	0.05	5.43	0.34*	
12	0- 10	5.04	0.09	0.10	0.01	5.10	0.06	
13	10- 60	3.78	0.06	0.09	0.03	3.86	0.08	
14	60-100	1.60	0.04	0.07	0.03	1.65	0.05	

Table IV--Continued

Soil no.	Depth (cm.)	Bremner's method (Kjeldahl)	Ammonium extracted from soil residue after calcination and digestion			Author's method	Difference between results of Bremner's method & author's method
			5N HF-N HCl-0.6N H ₂ SO ₄	40% HF	Differences		
Slate alluvial soils							
Yung-an, Chihu							
15	0- 40	6.32	0.20	0.24	0.04	6.62	0.30*
16	40- 90	5.54	0.24	0.22	0.02	5.76	0.22
17	90-100	6.40	0.21	0.20	0.01	6.73	0.33*
18	0- 30	3.20	0.07	0.10	0.03	3.29	0.09
19	30- 80	6.08	0.24	0.27	0.03	6.49	0.41*
20	80-100	4.78	0.30	0.30	0.00	5.06	0.28
Chung-hsi, Chihu							
21	0- 30	4.56	0.14	0.15	0.01	4.73	0.17
22	30- 60	6.72	0.34	0.32	0.02	7.12	0.40*
23	60-100	5.56	0.16	0.19	0.03	5.69	0.13
Hsin-tso, Pingtung							
24	0- 35	4.19	0.09	0.11	0.02	4.26	0.07
25	35- 75	5.52	0.07	0.09	0.02	5.56	0.04
26	75-100	4.96	0.11	0.08	0.03	5.06	0.10
27	0- 40	1.84	0.12	0.11	0.01	1.93	0.09
28	40-100	5.92	0.20	0.23	0.03	6.18	0.26
Wan-tan, Pingtung							
29	0- 15	4.88	0.27	0.29	0.02	5.21	0.33*
30	15- 45	4.64	0.30	0.26	0.04	4.91	0.27
31	45- 80	3.00	0.13	0.14	0.01	3.19	0.19

Table IV--Continued

Soil no.	Depth (cm.)	Bremner's method (Kjeldahl)	<u>Ammonium extracted from soil residue after calcination and digestion</u>			Differences	Author's method	Difference between results of Bremner's method & author's method
			$\frac{5N}{0.6N}$ HF-HCl- H_2SO_4		40% HF			
<u>Slate alluvial soils</u>								
Hou-pu, Nanchou								
32	0- 20	7.00	0.19	0.22	0.03	6.84	0.16	
33	20- 55	5.01	0.31	0.36	0.05	5.31	0.30*	
34	55-100	6.81	0.15	0.18	0.03	6.91	0.10	
35	0- 45	6.52	0.30	0.31	0.01	6.28	0.24	
36	45- 60	2.40	0.17	0.19	0.02	2.53	0.13	
37	60-100	3.52	0.13	0.16	0.03	5.70	0.18	
Hou-pi-tso, Nanchou								
38	0- 20	7.24	0.44	0.48	0.04	7.09	0.15	
39	20- 60	4.28	0.29	0.34	0.05	4.54	0.26	
40	60-100	4.08	0.24	0.29	0.05	4.29	0.21	
41	0- 40	3.96	0.22	0.24	0.02	4.26	0.30*	
42	40- 60	5.12	0.25	0.29	0.04	5.45	0.33*	
<u>Clay-sandstone alluvial soils</u>								
Tiao-chi-lin, Chiaotou								
43	0- 30	6.99	0.69	0.68	0.01	7.31	0.32*	
44	30- 65	5.37	0.59	0.61	0.02	5.53	0.16	
45	65-100	5.01	0.58	0.62	0.04	5.11	0.10	
Chung-tzu-lin, Chiaotou								
46	0- 30	8.93	0.31	0.29	0.02	9.10	0.17	
47	30- 60	7.33	0.30	0.33	0.03	7.39	0.06	
48	60-100	6.80	0.24	0.27	0.03	7.16	0.36*	

Table IV--Continued

Soil no.	Depth (cm.)	Bremner's method (Kjeldahl)	<u>Ammonium extracted from soil residue after calcination and digestion</u>				Difference between results of Bremner's method & author's method
			5N HF- N HCl- 0.6N H ₂ SO ₄	40% HF	Differ- ences	Author's method	
<u>Coral limestone alluvial soils</u>							
Chiu-kuei, Chiaotou							
49	0- 35	7.89	0.23	0.26	0.03	8.18	0.29*
50	35- 60	6.65	0.20	0.21	0.01	6.78	0.13
51	60-100	6.14	0.26	0.29	0.03	6.32	0.18
52	0- 15	7.46	0.31	0.32	0.01	7.83	0.37*
53	15- 85	6.41	0.25	0.27	0.02	6.55	0.14
54	85-100	5.33	0.26	0.29	0.03	5.45	0.12
Chung-chu, Hsiaokang							
55	0- 40	5.76	0.31	0.32	0.01	6.06	0.30*
56	40- 90	5.04	0.21	0.19	0.02	5.26	0.22
57	90-100	4.86	0.19	0.24	0.05	4.94	0.08
58	0- 40	5.76	0.24	0.28	0.04	6.15	0.39*
59	40- 90	3.52	0.15	0.21	0.06	3.77	0.25
60	90-100	5.36	0.26	0.26	0.00	5.65	0.29*
Nan-chu, Hsiaokang							
61	0- 30	7.40	0.38	0.40	0.02	7.25	0.15
62	30- 60	6.24	0.30	0.34	0.04	6.59	0.35*
63	60-100	3.52	0.16	0.21	0.05	3.79	0.27
64	0- 35	8.08	0.34	0.36	0.02	7.81	0.27
65	35- 70	7.21	0.28	0.34	0.06	7.51	0.30*
66	70-100	5.04	0.22	0.25	0.03	5.32	0.28

Data were average of 3 replications.

* Significant at 0.05 level.

Table IV showed that the total nitrogen values determined by the author's method were 0.03 to 0.41 me. per 100 g. soil higher than those determined by the Bremner method. The difference between the results of these two methods was significant on 21 soil samples. Table IV also showed that the total nitrogen content of the clay-sandstone alluvial soil and coral-limestone alluvial soil was considerably higher than that of the slate alluvial soil and the lateritic soil. In all instances the total nitrogen decreased with depth. The content of total nitrogen in the soils amounted to 1.93 to 9.10 me. per 100 g. soil in the surface soils and 1.65 to 7.51 me. per 100 g. soil in the subsoils. The higher values for total nitrogen in the surface soil was undoubtedly due to their high content of organic matter (Table V) and heavy application of ammonium fertilizers (73).

III. Study of ammonium fixing capacity

The purpose of this study was two fold: 1. to determine the amount of fixed ammonium in four representative Taiwan soil profiles, and 2. to determine the amount of fixation of ammonium derived from three different carriers of ammonium at various concentrations.

1. Determination of the amount of fixed ammonium in four representative Taiwan soil profiles

A. Method of investigation

Twelve soil samples of four profiles of Taiwan soils were used for study. Ten g. each, was pretreated with 10 ml. $\underline{\text{N}}$ $(\text{NH}_4)_2\text{SO}_4$ solution, followed by heating at 110°C for 24 hours (1). Then the sample was shaken with 20 ml. water, filtered through Whatman no. 1 filter-paper, and dried in oven at 50°C (42). At last, its content in

Table V. Pertinent characterization data of soils of the four profiles

Soil profile no.	Soil layer (cm.)	Mechanical analysis Clay	Silt	Sand	pH	Organic matter	Exchange- able K	Clay mineral*
		%	%	%		%	me.	
<u>Lateritic soils</u>								
Shan-tzu-chiao, Taichung								
1	0- 30	23	34	43	5.6	0.77	0.18	I, M, Q
	30- 50	41	26	33	4.3	0.46	0.12	I, M
	50-100	47	24	29	4.3	0.43	0.09	I, M
<u>Slate alluvial soils</u>								
Erh-lin, Chihu								
2	0- 30	24	48	28	8.2	1.13	0.05	I, M, V, C
	30- 70	35	57	8	8.1	0.74	0.03	I, M, V, C
	70-100	44	53	3	8.1	0.63	0.03	I, M, V, C
<u>Clay-sandstone alluvial soils</u>								
Tiao-chi-lin, Chiaotou								
3	0- 30	70	21	9	7.7	1.68	0.28	I, M, V, C
	30- 65	70	22	8	8.1	0.77	0.21	I, M, V, C
	65-100	62	30	8	8.3	0.62	0.16	I, M, V, C
<u>Coral limestone alluvial soils</u>								
Chung-chu, Hsiaokang								
4	0- 40	38	46	16	8.0	1.02	0.12	I, M, C
	40- 90	50	42	8	8.2	0.72	0.09	I, M, C
	90-100	64	32	4	8.3	0.39	0.15	I, M, C

* I = illite, M = hydrous mica, V = vermiculite, C = chlorite,
Q = quartz.

fixed ammonium was determined according to the method previously described.

B. Discussion of results

The results (Table VI) showed that more ammonium was fixed by the slate alluvial soils and clay-sandstone alluvial soils than by the coral limestone alluvial soils and the lateritic soils. The greater capacity of slate alluvial soils and clay-sandstone alluvial soils for the fixation of nonexchangeable ammonium as compared to coral limestone alluvial soils and the lateritic soils was apparently associated with the different organic matter content and the composition of clay minerals in these soils. Slate alluvial soils and clay-sandstone alluvial soils contain vermiculite and it is known that vermiculite minerals fix quantities of NH_4^+ greatly in excess of the amounts fixed by other minerals (79).

The capacity for the fixation of nonexchangeable ammonium depends also on soil texture. The 12 soil samples studied differed in texture, and their capacity to fix nonexchangeable ammonium was not the same (Table V and VI). The finer-textured soils have higher capacity for the fixation of such ammonium in the nonexchangeable form than do those of coarser texture.

The amount of fixed ammonium in 12 soil samples was 1.35 to 2.19 me. per 100 g. soil in the surface soils and 1.44 to 2.97 me. per 100 g. soil in the subsoils. Allison (3), Hanway (37), Nommik (56) and Stevenson (67) found that the capacity for fixing ammonium by the upper soil layer was usually much lower than that of the deeper soil layers. In the opinion of Allison et al. (3), the reason for

Table VI. Ammonium fixing capacity of soils of four soil profiles (me./100g. soil)#

Soil profile no.	Soil layer (cm.)	Total N	Natural fixed NH_4^+-N	% of total N	Total NH_4^+-N fixing capacity	Capacity for additional fixation of NH_4^+-N
<u>Lateritic soils</u>						
Shan-tzu-chiao, Taichung						
1	0- 30	4.07	1.26	32.30	1.35	0.09
	30- 50	3.91	1.38	28.33	1.52	0.14
	50-100	3.13	1.34	23.36	1.44	0.10
<u>Slate alluvial soils</u>						
Erh-lin, Chihu						
2	0- 30	6.94	2.06	33.69	2.19	0.13
	30- 70	6.09	2.16	28.19	2.26	0.10
	70-100	5.43	2.44	22.25	2.78	0.34
<u>Clay-sandstone alluvial soils</u>						
Tiao-chi-lin, Chiaotou						
3	0- 30	7.31	1.97	37.11	2.11	0.14
	30- 65	6.24	2.27	27.49	2.36	0.09
	65-100	5.11	2.50	20.44	2.97	0.47
<u>Coral limestone alluvial soils</u>						
Chung-chu, Hsiaokang						
4	0- 40	6.06	1.68	36.07	1.72	0.04
	40- 90	5.26	1.57	33.50	1.58	0.01
	90-100	4.94	2.01	24.58	2.11	0.10

Data were average of 3 replications.

this was that the fixation capacity of the upper soil layer was already saturated to a certain degree by potassium and ammonium.

2. Determination of the amount of ammonium fixed from three different carriers at various concentrations

A. Method of investigation

Soil sample no. 45 characterized with high ammonium fixation capacity was selected for test of fixation of ammonium derived from three carriers; namely, ammonium sulphate, diammonium phosphate and ammonium hydroxide at various concentrations. Then, 10 g. soil samples were treated with 10 ml. of each of the three carriers at various rates separately, and then heated at 110°C for 24 hours (1). Then the soil samples were shaken with 20 ml. water, filtered and dried in an oven at 50°C . The amount of ammonium fixed in each of the soils was determined by the author's proposed method as described above. The difference between the total fixed ammonium and the natural fixed ammonium was the amount of ammonium fixed due to the treatment.

B. Discussion of results

The results, given in Table VII, showed that soil sample no. 45 possessed high ammonium fixation capacity with the three carriers of ammonium. The fixation of ammonium was low, when the added solution was dilute. It increased remarkably, when the ammonium in the added solution was increased from 30 me. to 40 me. From thence on, the increase in concentration of the added ammonium solution did not appreciably affect fixation of ammonium. The three different carriers of ammonium, did not produce differences in the amount of fixed ammonium in the soil. There are at least three probable reasons for the failure

Table VII. Ammonium fixation as influenced by kinds of carriers and levels of NH_4^+-N (me./100g. soil)#

NH_4^+ added@	$(\text{NH}_4)_2\text{HPO}_4$		$(\text{NH}_4)_2\text{SO}_4$		NH_4OH	
	Total fixed NH_4^+-N	Additional fixed NH_4^+-N	Total fixed NH_4^+-N	Additional fixed NH_4^+-N	Total fixed NH_4^+-N	Additional fixed NH_4^+-N
0	2.50	-	2.50	-	2.50	-
5	2.53	0.03	2.54	0.04	2.52	0.02
10	2.55	0.05	2.55	0.05	2.54	0.04
20	2.59	0.09	2.57	0.07	2.54	0.04
30	2.64	0.14	2.65	0.15	2.58	0.08
40	2.81	0.31	2.89	0.39	2.83	0.33
50	2.82	0.32	2.81	0.31	2.82	0.32
60	2.85	0.35	2.82	0.32	2.89	0.39
70	2.82	0.32	2.83	0.33	2.82	0.32
80	2.84	0.34	2.86	0.36	2.84	0.34
90	2.85	0.35	2.84	0.34	2.85	0.35
100	2.87	0.37	2.85	0.35	2.86	0.36

Data were average of 3 replications.

@ Ten g. soil was treated with 10 ml. of three ammonium sources at various rates.

of soils to fix excessive amounts of ammonium even though they contain illite, hydrous mica and vermiculite: (a) the clay minerals may already be nearly saturated with ammonium, since its formation proceeds continuously in soil, (b) ammonium entrance may be blocked by the prior entrance of potassium, and (c) organic matter may also partly block fixation.

IV. Study of ammonium fixation under different conditions

The purpose of this study was to determine the amount of applied ammonium fixed in soil under different conditions, namely; moist, frozen and oven-dried.

Several samples of soil no. 45 in the amount of 10 g. each were placed in beakers, and allowed to equilibrate with 10 ml. ammonium sulphate solution at different concentrations. The sample to be kept under moist condition was stored in a refrigerator (5° C) for 7 days. The sample to be kept under frozen conditions was placed in a subzero (-20° C) freezer for 7 days. The sample to be kept under oven-dried condition was dried in an oven at 60° C for 7 days. After 7 days, each sample was shaken with 20 ml. water in order to filter through Whatman no. 1 filter paper and dried in oven at 50° C (42). The sample of each treatment was analyzed for total fixed ammonium by the author's proposed method as described previously. The difference between the total fixed ammonium and the natural fixed ammonium represented the amount of added ammonium fixed under different conditions.

The results in Table VIII showed that soil no. 45 did fix a little ammonium under moist and frozen conditions, but when oven-dried

Table VIII. Fixation of applied ammonium under moist, frozen and oven-dried conditions (me./100g. soil)#

NH_4^+ added	Moist		Frozen		Oven-dried	
	Total fixed NH_4^+-N	Additional fixed NH_4^+-N	Total fixed NH_4^+-N	Additional fixed NH_4^+-N	Total fixed NH_4^+-N	Additional fixed NH_4^+-N
5	2.51	0.01	2.52	0.02	2.54	0.04
10	2.53	0.03	2.53	0.03	2.53	0.03
20	2.53	0.03	2.52	0.02	2.55	0.05
30	2.54	0.04	2.52	0.02	2.61	0.11
40	2.53	0.03	2.53	0.03	2.64	0.14
50	2.59	0.09	2.57	0.07	2.70	0.20
60	2.56	0.06	2.56	0.06	2.69	0.19
70	2.55	0.05	2.56	0.06	2.73	0.23
80	2.54	0.04	2.54	0.04	2.78	0.28
90	2.56	0.06	2.54	0.04	2.87	0.37
100	2.55	0.05	2.56	0.06	2.79	0.29

Data were average of 3 replications.

it fixed a substantial amount. When 5 to 100 me. per 100 g. soil of ammonium was added, 2.51 to 2.59 me. per 100 g. was fixed under moist condition. Freezing of the soil after the addition of ammonium resulted in as much fixation as that kept under moist condition did. In the opinion of Walsh and Murdock (69), the lower values of fixed ammonium under frozen condition might have been due to the fact that the soil and ammonium had not been allowed to equilibrate enough before the sample was placed in the freezer. A number of investigators (2, 60, 63, 67) showed that the fixation of ammonium, as well as potassium, by soils increased as the soil dried out in the presence of ammonium salt and, especially, when it was heated to 100° C. But in many cases some soils could retain considerable amount of ammonium in a nonexchangeable form (19, 65). The data presented in Table VIII also showed that the soil under test fixed 2.53 to 2.87 me. per 100 g. under oven-dried condition. Since the clay minerals in this soil were illite, hydrous mica and vermiculite (Table V), the effect of heat was probably due chiefly to the increased contraction of the mineral lattice by the more thorough drying.

V. Release of fixed ammonium as affected by added potassium

The purpose of this study was to determine the availability of fixed ammonium to sugar cane as affected by added potassium.

Three hundred g. of soil sample no. 45 known as high fixation capacity was saturated with 300 ml. $\underline{\text{N}} (\text{NH}_4)_2\text{SO}_4$ solution and heated at 110° C for 24 hours (1). Then 600 ml. water was added and filtered and at last dried in an oven at 50° C (42). A mixture consisting of 300 g.

NH_4^+ -saturated soil with equal volume of silica sand (> 1 mm.) was heated at 400°C (within $\pm 20^\circ \text{C}$) for 36-40 hours. The calcined soil was then leached with $\underline{\text{N}}$ CaCl_2 solution, followed by $0.1 \underline{\text{N}}$ CaCl_2 - MgCl_2 mixture (1, 2), and then with water until the filtrate responded slightly to test for potassium and chloride. Then the soil and quartz sand mixture was leached with Hoagland solution (41) without nitrogen and potassium. The soil mixture was placed in a 1-liter polyethylene pot prior to use.

Two-eye cuttings of the sugar cane variety N:Co 310, uniform in size (125-135 g. per seed piece), were planted in moist quartz sand. When the young shoots had grown to 8 to 12 cm. in height with well-developed roots, they were carefully washed from the quartz sand with tap water. One end of the sugar cane cutting was planted in the treated soil mixture contained in the 1-liter polyethylene pot, while the other end in a 1-liter polyethylene pot filled with Hoagland solution (41), modified to contain 0.01-0.02 me. of K and no N. The nutrient solution showed a pH value of 5.5. In this test, three treatments were made: (a) soil without addition of potassium and inoculation, (b) soil amended with 1.5 me. K per 100 g. of soil and inoculated, and (c) soil inoculated only. Each treatment was replicated three times. One ml. of Hsi-chu, Hsiaokang Hsiang soil extract known to contain active nitrifying flora (78) was added to the inoculated soils. The amount of ammonium in the inoculant was 0.28 me. Soil moisture was maintained at near the moisture equivalent. Each polyethylene pot was covered with black polyethylene paper in order to avoid sunlight that might interfere with the experiment. At first, the nutrient solution

was changed once every two weeks. As the plants developed, the nutrient solution was renewed each week. On July 5, 1966, a photograph of the plant of each of the treatments was taken (Fig. 1).

Sixty days after planting (July 6, 1966), the plants were harvested. The leaves and roots were carefully cut, oven-dried at 80° C and then weighed. The soil mixture was leached with 1500 ml. $\underline{\text{N}}$ K_2SO_4 solution (64), the leachate was analyzed for available nitrogen, including exchangeable ammonium and nitrate, by Nesslerization following reduction of NO_3^- to NH_4^+ (42). The quartz was separated from the soil by means of a 0.5 mm. (32 mesh) sieve. Fixed ammonium in the soil was determined by the author's method as described above. The results are shown in Table IX and X.

The results of this test indicated that soil sample no. 45 had a high ammonium fixation capacity. The content of fixed ammonium was 8.40 me. per 300 g. soil in the 1-liter polyethylene pot. Release of fixed ammonium ranged from 2.86 to 25.83 per cent for soils with three treatments. The tested soils, inoculated with nitrifying flora, showed 25.83 per cent release of the fixed ammonium; however, as 1.5 me. K per 100 g. soil was added to the soil, the amount of fixed ammonium released decreased to 5.00 per cent. The untreated soil always gave the lowest value.

Table X showed that the average total weight of the sugar cane on the untreated soil was the smallest. The addition of K suppressed the growth of the plant to 1/3 on the inoculated soils.

It was evident from the present investigation, that the availability of the fixed ammonium depends upon the inoculation of nitrifying

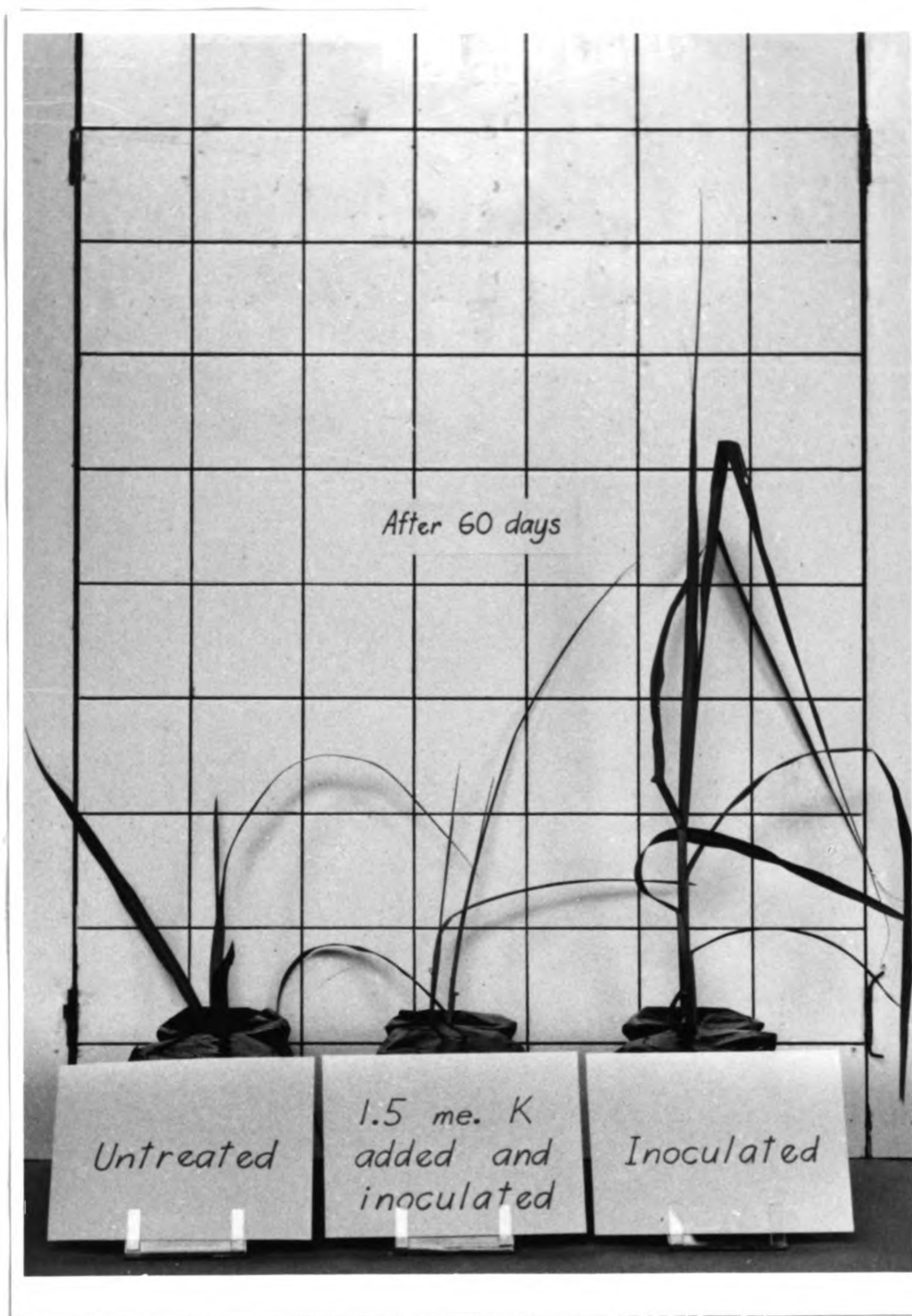


Fig. 1.--Response of sugar cane to fixed ammonium in Tiao-chi-lin soil with and without K addition or inoculation with nitrifying microflora.

Table IX. Release of fixed ammonium in soil as affected by added potassium (me./pot)#

Treatments	Fixed NH_4^+-N in 300 g.	NH_4^+-N in inocu- lant	Total NH_4^+-N	Available N eluated with $\text{N K}_2\text{SO}_4$	% of fixed NH_4^+-N released
Untreated	8.40	-	8.40	0.24	2.86
1.5 me. K added and inoculated	8.40	0.28	8.68	0.70	5.00
Inoculated	8.40	0.28	8.68	2.45	25.83

Data were average of 3 replications.

Table X. Effect of added K on the yields of sugar cane plants (g./pot)#

Treatments	Dry weight of sugar cane plant			
	Leaves	Roots	Total	Index
Untreated	2.8	1.0	3.8	23.75
1.5 me. K added and inoculated	3.8	1.8	5.6	35.00
Inoculated	12.4	3.6	16.0	100.00

Data were average of 3 replications.

flora and the addition of potassium. Soil extract of Hsi-chu, Hsiaokang Hsiang soil used for inoculation has been reported by Yeh and Jen (78). When 1.5 me. K per 100 g. soil was added, the amount of fixed ammonium in the tested soil that was nitrified decreased. Thus, the decrease in nitrification observed with the tested soil must have been due to the blocking effect of potassium on the release of the fixed ammonium. It has also been suggested by Hanway and Scott (37) and by Nommik (56) that the exchangeable potassium level in the soil may affect nitrification rates of fixed ammonium, owing to the blocking effect of the potassium ion.

SUMMARY

A procedure has been suggested for the determination of fixed ammonium in soils. The organic matter and exchangeable ammonium of the soil were removed by Mogilevkina's calcination method and the last fraction of fixed nitrogen contained in the mineral residue after Kjeldahl digestion was released with concentrated HF. A comparison of the proposed method with Mogilevkina's modified Bremner method and a recovery test of nitrogen from ammonium sources with the proposed method have been made. This proposed method has been found dependable and accurate.

A method for the determination of total nitrogen in soils has also been suggested. The method involves destroying mineral residues after Kjeldahl digestion and releasing fixed ammonium therein with concentrated HF. A comparison of the proposed method with Bremner's modified Kjeldahl method was studied. The proposed method gave much higher values than Bremner's method did. The reliability and significance of the results obtained by the proposed method were discussed. Since fixed ammonium is, at least, partially available to plants, and is a potential source of soil nitrogen, it should be included in the analysis of total soil nitrogen. The main reasons for the proposed method are an improvement over the previous methods: (a) higher values for fixed and total N appear to be due to more complete release of fixed ammonium, and (b) fixed ammonium can be a significantly available source of nitrogen for plants.

The distribution of natural fixed ammonium in 66 soil profiles in Taiwan was found to be 1.08 to 2.10 me. per 100 g. in the surface soils and 0.95 to 2.50 me. per 100 g. in the subsoils.

The ammonium fixing capacity of 12 Taiwan soil profiles was 1.35 to 2.19 me. per 100 g. in the surface soils and 1.44 to 2.97 me. per 100 g. in the subsoils. The capacity for fixation of ammonium by the surface soil was lower than that of the subsoils. The fixation of ammonium in tested soil samples was associated with the presence of illite, hydrous mica, and vermiculite. These minerals were chiefly found in the clay fraction of the soils. For this reason the distribution of fixed ammonium in the soil profile mostly corresponded to the distribution of clay in soils.

Soil sample no. 45 known as having high fixation capacity was selected for test of fixation of ammonium with $(\text{NH}_4)_2\text{HPO}_4$, $(\text{NH}_4)_2\text{SO}_4$ and NH_4OH . When 5-30 me. NH_4^+ per 100 g. soil of ammonium salts was added to the soil, the fixation values varied between 2.52 and 2.65 me. per 100 g. soil; when 40-100 me. was added, the values were 2.81 to 2.87 me. The differences due to rates of application with three ammonium sources were statistically not significant.

The ammonium fixing capacity of soil sample no. 45 under moist, frozen and oven-dried conditions was also determined. When the soil was moist and frozen in presence of various rates of an ammonium salt the fixation values were between 2.51 and 2.59 me. per 100 g. soil; when the soil was oven-dried, the quantity fixed increased to 2.53 and 2.87 me. per 100 g. soil. The clay minerals of the soil contain vermiculite that was known to fix ammonium under both moist and dry

conditions. Drying of the soil, especially with heat, favored fixation. The low ammonium fixing capacity of the soil sample no. 45 was probably due to partial saturation of ammonium and potassium in the clay minerals of the soil.

The effect of added K on the availability of fixed ammonium uptake by sugar cane was investigated. When soil was inoculated with nitrifying flora, 25.83 per cent of the fixed ammonium was released in 60 days. When 1.5 me. K was added to the soil, the amount of fixed ammonium released decreased to 5.00 per cent. This could be explained by the fact that the added K interfered with the release of the NH_4^+ in the soil because it blocked the release of fixed ammonium.

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