# Identification of the causes of subsoil ammonium accumulations in southeastern Queensland

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## Abstract
Unusually high concentrations of exchangeable-$NH_4^+$ (up to 270 kg-N/ha) were observed in a Vertisol below 1 m in southeast Queensland. This study aimed to identify the source of this $NH_4^+$. Preliminary sampling of native vegetation and cropping areas had found that elevated $NH_4^+$was only present under cropped soil, indicating that clearing was linked to the $NH_4^+$formation. Mechanisms of $NH_4^+$formation that may have occurred in the subsoil after clearing were hypothesised to be a) mineralisation of organic-N; b) $NO_3^-$ reduction to $NH_4^+$; and/or c) the release of fixed-$NH_4^+$. In addition it was proposed that nitrification was inhibited in the subsoil, and that this allowed any $NH_4^+$formed to accumulate over time. Incubation experiments to examine nitrification rates revealed that nitrification was undetectable, and appeared to be limited by a combination of subsoil acidity and low numbers of nitrifying organisms. Mineralisation studies also revealed that the mineralisation of organic-N was undetectable, and that mineralising organisms were limited by acidity. A small amount of nitrate ammonification could be observed with the aid of a $^{15}N$ tracer if the soil was waterlogged. However, this $NH_4^+$was insufficient to account for the overall $NH_4^+$accumulation, and these waterlogged conditions were not observed in the field. Concentrations of fixed- $NH_4^+$ measured were also too low to have been responsible for the accumulation of exchangeable-$NH_4^+$. It was concluded that none of the proposed hypotheses of $NH_4^+$formation could account for the $NH_4^+$accumulation observed.

## Introduction
In a Vertisol soil in southeast Queensland, high concentrations of exchangeable ammonium ($NH_4^+$ )(>270 kg-N/ha) have been observed below 1m (Hossain *et al.* 1996; Page *et al.* 2002). This $NH_4^+$ is considered unusual for two reasons. Firstly, no obvious source of $NH_4^+$ production can be identified. Secondly, it is unusual that $NH_4^+$concentrations have built up, as nitrification occurs rapidly in most agricultural soils (Tate 2000).It is known that high suboil $NH_4^+$concentrations are not ubiquitous throughout the region, but nor are they an isolated occurrence (Page 2002). Understanding the mechanism of $NH_4^+$ formation may help to identify other areas of accumulation that may be a useful source of nitrogen for agriculture.

One important feature of the subsoil $NH_4^+$ is that it appears under areas of cultivation, but not adjacent areas of native vegetation (Page *et al.* 2002). This would suggest that the clearance of native vegetation has triggered some change that has led to the formation of $NH_4^+$. The removal of native vegetation would have created numerous changes within the soil environment. For example, it would have caused the death of any root material associated with the native vegetation, decreased nutrient extraction from the deep subsoil, and increased water movement through the profile due to decreased transpiration.

The above changes could have triggered $NH_4^+$production via a number of pathways. For example, mineralisation of either native vegetation root material killed after clearing, or dissolved organic-N leached into the subsoil could have released $NH_4^+$. Given the relatively high clay content of this soil, the greater movement of water into the subsoil may also have resulted in increased periods of waterlogging. If waterlogging lowered the soil redox potential sufficiently, nitrate ammonification (the direct reduction of $NO_3^-$ to $NH_4^+$) may have occurred, and $NH_4^+$ accumulated due to the absence of deep nutrient extraction. Similarly the absence of deep nutrient extraction may have allowed any exchangeable-$NH_4^+$ released from the fixed mineral fraction to have accumulated.

It should also be noted, that the increased movement of water may have resulted in direct leaching of exchangeable-$NH_4^+$. However, any increase in $NH_4^+$leaching is likely to be small because the site has previously been unfertilised, has low levels of exchangeable-$NH_4^+$in the surface soil, is unirrigated, and has a mean annual rainfall of only 630 mm/yr. Because of this, and because of the difficulties associated



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with examining the leaching of very small amounts of $NH_4^+$ in the field, this pathway of $NH_4^+$ accumulation was not examined.

It was the aim of this study to determine whether mineralisation, nitrate ammonification or fixed- $NH_4^+$ release were responsible for the formation of exchangeable-$NH_4^+$ at this site. In addition the reason for the apparent absence of subsoil nitrification was also investigated.

## Methods

*Site Description*

The study site was located in southeast Queensland (26°47'S, 150°53'E). The area was originally under Brigalow (*Acacia harpophylla*) vegetation, but cleared during the mid 1930s and used for dryland agriculture, predominantly wheat cropping, ever since. The soil was classified as a thermic, Typic Chromustert or Grey Vertosol. Relevant site characteristics are summarised in Tables 1 and 2. Regular application of N fertiliser has not occurred.

**Table 1. Soil profile characteristics reproduced from Dalal *et al.* (1995)**

| Depth (m) | Bulk Density ($Mg/m^3$) | Sand (%) | Silt (%) | Clay (%) |
|---|---|---|---|---|
| 0-0.1 | 1.24 | 27 | 17 | 56 |
| 0.1-0.2 | 1.27 | 27 | 16 | 57 |
| 0.2-0.3 | 1.28 | 28 | 15 | 57 |
| 0.3-0.6 | 1.36 | 25 | 16 | 59 |
| 0.6-0.9 | 1.42 | 20 | 17 | 63 |
| 0.9-1.2 | 1.43 | 19 | 16 | 65 |
| 1.2-1.5 | 1.45 | 19 | 15 | 66 |

**Table 2. Summary of site characteristics for cropping and native vegetation sites. Organic-C and N values were obtained from 5 bulked soil cores. The remaining values are averages from 5 separate cores. Values in brackets are standard deviations.**

| Depth (m) | Exchangeable-$NH_4^+$ (mg/kg) | | Organic-C (%) | | Organic-N (%) | | pH | | EC (dS/m) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Native | Crop | Native | Crop | Native | Crop | Native | Crop | Native | Crop |
| 0-0.3 | 1.7 (0.4) | 2.5 (0.5) | 0.9 | 0.38 | 0.10 | 0.05 | 7.9 | 8.8 | 0.4 | 0.2 |
| 0.3-0.6 | 0.5 (0.4) | 0.3 (0.3) | 0.33 | 0.23 | 0.04 | 0.03 | 8.4 | 8.6 | 1.2 | 0.5 |
| 0.6-0.9 | 0.3 (0.1) | 0.4 (0.1) | 0.25 | 0.16 | 0.03 | 0.02 | 7.7 | 7.9 | 1.5 | 0.5 |
| 0.9-1.2 | 0.6 (0.4) | 2.7 (2.1) | 0.25 | 0.18 | 0.02 | 0.02 | 4.9 | 5.6 | 1.5 | 0.8 |
| 1.2-1.5 | 0.5 (0.1) | 14.2 (5.4) | 0.18 | 0.18 | 0.02 | 0.01 | 4.5 | 4.9 | 1.5 | 1.0 |
| 1.5-1.8 | 0.5 (0.2) | 18.9 (3.1) | 0.13 | 0.15 | 0.01 | 0.01 | 4.4 | 4.5 | 1.6 | 1.1 |
| 1.8-2.1 | 0.9 (0.2) | 16.1 (2.9) | 0.11 | 0.15 | 0.01 | 0.01 | 4.3 | 4.4 | 1.6 | 1.3 |
| 2.1-2.4 | 0.5 (0.2) | 11.4 (2.1) | 0.14 | 0.11 | 0.01 | 0.01 | 4.3 | 4.5 | 1.7 | 1.6 |
| 2.4-2.7 | 0.5 (0.4) | 8.9 (1.6) | 0.12 | 0.11 | 0.01 | 0.01 | 4.3 | 4.4 | 1.7 | 1.6 |
| 2.7-3.0 | 0.9 (0.4) | 4.9 (2.2) | 0.09 | 0.12 | 0.01 | 0.01 | 4.2 | 4.3 | 1.7 | 1.7 |

*Nitrification studies*

Five soil cores were collected from between 1.2 and 3.0 m along a 100 m transect in an area of native vegetation adjacent to the cropped area where exchangeable-$NH_4^+$ had accumulated. This soil was sieved in a field moist state to <5mm, and 50 g weighed into 1L containers. To determine the environmental conditions inhibiting nitrification in the subsoil, the following treatments were applied in a two level (i.e. present/absent) factorial design. The pH was increased from 4.4 to 7.0 using $CaCO_3$, the subsoil was inoculated with surface soil organisms by adding 0.5 g of surface soil, and the electrical conductivity of the soil was reduced from 1.6 to 0.5 dS/m by leaching. Each treatment was replicated five times. An $NH_4^+$ solution was added to all samples to bring total concentrations to 50 mg-N/kg (initial soil $NH_4^+$ and $NO_3^-$ concentrations were <1 mg/kg). Soil was then incubated at 22°C and 70% humidity. Destructive samplings were conducted at 20, 60 and 180 days and $NO_3^-$ measured.

*Mineralisation studies*

Root measurement

To estimate the amount of N contained within native vegetation roots, roots were washed from five soil cores collected across the native vegetation site, dried at 60°C, and weighed. The average weight of roots collected was then used in combination with their total-N content to estimate the total quantity of N contained in roots throughout the soil profile.

Waterlogged incubation

A waterlogged incubation was used to assess the quantity of potentially mineralisable N present in the subsoil at the time of clearing, using soil from the 1.5 to 3 m layer of the native vegetation site. Waterlogged incubations were conducted as described in (Waring and Bremner 1964), except that soil was incubated at 40ºC for 1 week. A series of treatments was also applied in a two level factorial design (i.e. present/absent) to examine environmental factors that may limit mineralisation. These treatments increased soil pH from 4.4 to 7 using $CaCO_3$, and inoculated the subsoil with surface soil microorganisms. In addition, glutamic acid ($C_5H_9NO_4$), was added at a rate of 250 mg-N/kg in order to determine the whether an easily mineralisable organic-N source could be broken down. Five replicates were used for each treatment. After incubation, the $NH_4^+$ concentration of samples was determined.

*Nitrate Ammonification*

Soil Redox Capacity

To determine whether the subsoil was reducing enough to allow nitrate ammonification, a field test for redox capacity was conducted at 3 locations in the area of cultivation and native vegetation. At each location a portion of soil between 1.75 and 1.80 m was immediately tested for redox capacity using a field test developed by Bartlett and James (1995).

Waterlogged incubation

To examine the potential for nitrate ammonification to occur in soil subjected to waterlogged conditions, 30 g of field moist soil from the 1.5 - 2.7 m layer of the cleared site was weighed into containers containing 30 mL of deionised water. Soil was then amended with $KNO_3$ enriched with 5% $N^{15}$ at a rate of 30 mg-N/kg. Extra samples were also placed under incubation for 50 days, after which time a solution of Fe(II) (as $FeSO_4$) was added to the soil to bring reduced iron concentrations to 100 mg/kg (in order to increase the rate of any abiotic nitrate ammonification). Samples were placed in sealed incubation jars that were flushed with N gas to maintain low oxygen conditions. At 0, 25, 50 and 75 days soil was sampled for redox status, exchangeable-$NH_4^+$ and -$NO_3^-$, and the $^{15}N$ enrichment of the exchangeable-$NH_4^+$ fraction. Treatments were replicated five times.

Fixed Ammonium

Fixed $NH_4^+$ was quantified to a depth of 3 m on the crop and native vegetation sites (Silva and Bremner 1966). Average profile fixed $NH_4^+$ concentrations were estimated from five replicate soil cores collected across the site that were bulked. In addition, to obtain an idea of site variability, individual replicates from the 1.8-2.1 m layer were analysed. Mineralogy of the clay fraction was also determined using x-ray diffraction.

Analytical Methods

Exchangeable-$NH_4^+$ and -$NO_3^-$ were extracted using a 2 M KCl solution. Ammonium was analysed using a colorimetric method based on the indo-phenol blue technique (Henzell *et al.* 1968), and $NO_3^-$ was reduced to $NO_2$- with hydrazine and a copper catalyst and the $NO_2^-$ produced measured using a procedure based on the Greiss-Ilosvay reaction (Bremner 1965). The $NH_4^+$ in those samples amended with organic-N was measured using steam distillation with MgO, due to interference of glutamic acid with the colorimetric technique (Bremner and Keeney 1966). Measurement of the $^{15}N$ enrichment of the exchangeable-$NH_4^+$ fraction was conducted by distilling a 20 mL aliquot of KCl extract with MgO and collecting the resulting distillate in 1 mL of saturated boric acid (Bremner and Keeney 1966). The $^{15}N$ content of samples was determined on a dual-inlet VG Isogas SIRAIO mass spectrometer. Electrical conductivity and pH were measured from a 1:5 soil:water extract. Organic carbon was measured using the Walkley-Black procedure (Walkley and Black 1934) with a colorimetric finish (Sims and Haby 1971).

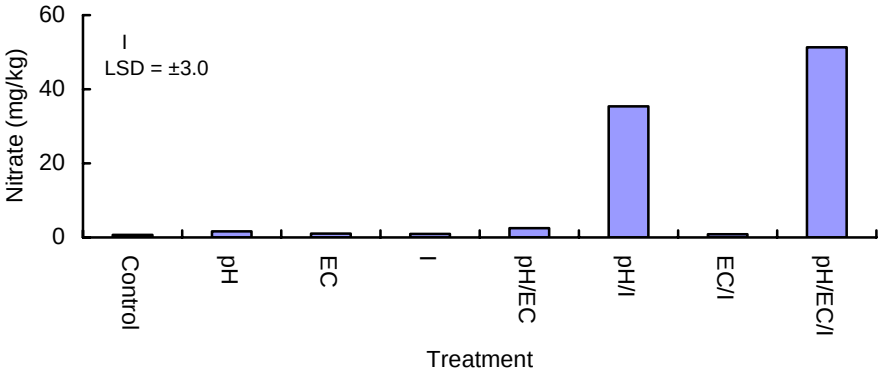
Total-N was extracted using a Kjeldahl digestion and $NH_4^+$ produced measured colorimetrically (Crooke and Simpson 1971).

**Results and Discussion**

*Nitrification Study*
At all sampling times during this incubation experiment, $NO_3^-$ concentrations were <1 mg/kg. This provides strong evidence that the rate of nitrification in this soil is extremely low. At the 180 day sampling period, inoculum, pH, and EC treatments had no significant effect (P>0.05) on the production of $NO_3^-$ in isolation (0). However, in combination, pH and inoculum treatments did significantly increase $NO_3^-$concentration, and when pH, EC and inoculum treatments were all added, a further increase in $NO_3^-$ production occurred (0).

The significant increases in $NO_3^-$concentration observed when inoculum/pH, or inoculum/pH/ EC treatments were added to the soil indicate three things. Firstly, the absence of nitrification without the addition of inoculum indicates that an active autotrophic nitrifying population must be largely absent from the subsoil. Secondly, the fact that nitrification only occurred when inoculum was added in combination with increased pH, indicates that the nitrifying organisms contained within the inoculum were inhibited by acidic conditions. Thirdly, the fact that a greater increase in $NO_3^-$ concentration was observed when inoculum was added in combination with pH and EC treatments (0), indicates that the microorganisms used as inoculum were also somewhat inhibited by the saline conditions at depth.

The effect of subsoil pH and salinity on nitrifying activity is likely because the organisms used in the inoculum were from the top 0-5 cm of the soil profile. This section of the profile is characterised by a pH of 6.5 and an EC of ~0.4 dS/cm. Nitrification is commonly inhibited at low pH (Chung and Zasoski 1993; Persson and Wiren 1995), and soil salinity (McClung and Frankenberger 1987; Murase *et al.* 1994; Rysgaard *et al.* 1999), and it is not surprising that when microorganisms from this horizon were exposed to the subsoil pH of 4.4 and an EC >1.5 dS/m, that nitrifying activity was inhibited. These results indicate that the ammonium observed in the subsoil has been able to accumulate due to a lack of nitrification, and that nitrification has not been able to occur due to an apparent absence of an active nitrifying population. Such a population may have been unable to establish in the subsoil due to inhibition from subsoil acidity, and to a lesser extent, subsoil salinity.




**Effect of pH, electrical conductivity (EC), inoculation (I) treatments, and their combinations on $NO_3^-$ concentrations (mg-N/kg) at the 180-day time period.**

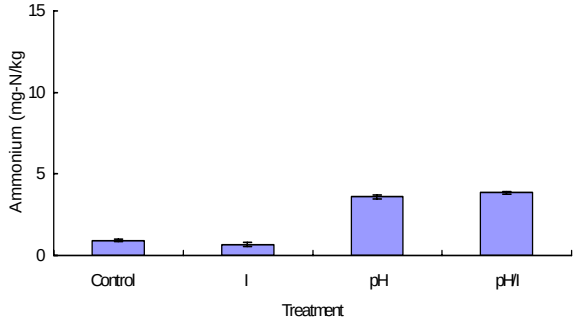
*Mineralisation Studies*
Root measurement
The average N concentration of Brigalow root material is presented in 0. These results show that the amount of N contained in Brigalow root material between 1.2 and 3 m (the area of subsoil $NH_4^+$accumulation) was approximately 90 kg-N/ha. The amount of exchangeable-$NH_4^+$ between 1.2 and 3 m was approximately 380 kg-N/ha (0). These results indicate that the mineralisation of native vegetation root material could not be the sole source of the exchangeable-$NH_4^+$.

**Table 3. Total-N concentration (mg-N/kg of soil) contained in Brigalow root biomass between 0 and 3.0 m (standard error in brackets).**

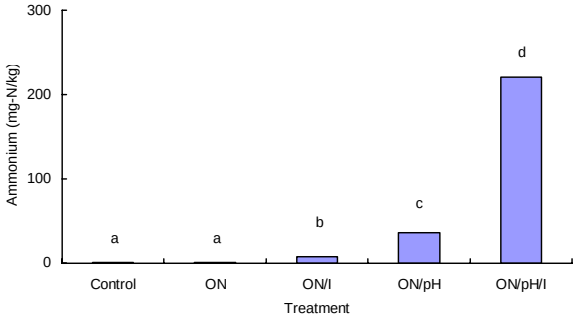
| Depth (m) | Total-N (mg-N/kg) |
|---|---|
| 0-0.3 | 159 (24) |
| 0.3-0.6 | 21 (2) |
| 0.6-0.9 | 12 (2) |
| 0.9-1.2 | 12 (6) |
| 1.2-1.5 | 4 (1) |
| 1.5-1.8 | 6 (1) |
| 1.8-2.1 | 3 (1) |
| 2.1-2.4 | 2 (1) |
| 2.4-2.7 | 2 (0) |
| 2.7-3.0 | 4 (1) |

Waterlogged incubations

Results from the waterlogged incubation showed that there was no significant increase in the $NH_4^+$ concentration of samples subjected to waterlogging compared to unincubated samples. The $NH_4^+$ concentrations of samples after the alteration of soil pH and the addition of inoculum are presented in 0. Increasing the soil pH resulted in a significant increase in $NH_4^+$ concentration, but the alteration of the microbial population had no significant effect on $NH_4^+$. Subsoil samples incubated in the presence of organic-N (without alteration of soil pH or microbial population), showed no significant increase in $NH_4^+$concentration (0). However, when organic-N was added in combination with pH and/or inoculation treatments, a significant increase in $NH_4^+$concentration was observed. The greatest amount of $NH_4^+$was produced when pH and inoculation treatments were used in combination.




**$NH_4^+$ concentration (mg-N/kg) of inoculation (I), and pH treatments. Vertical bars indicate standard errors.**




**$NH_4^+$ concentration (mg-N/kg) of soil incubated with added organic-N (ON), inoculum (I) and increased pH. Bars with the same letter are not significantly different (P>0.05).**

The failure to observe any mineralisation of either *in situ* or added organic material while the subsoil was in its natural condition indicates that the ability of the indigenous microbial population to conduct mineralisation is severely limited. This indicates that no organic-N, whether it is present *in situ* or transported to the subsoil during leaching events is likely to be converted to $NH_4^+$ at a rate great enough to account for the accumulation of $NH_4^+$observed. The significant increase in $NH_4^+$production observed when soil pH was increased (0 and 0) indicates that subsoil acidity is at least partly responsible for the slow rate of mineralisation at this site. The depression of mineralisation due to soil acidity have been observed in a number of studies (Curtin *et al.* 1998; Sapek 1997).

*Nitrate ammonification studies*

Redox Capacity

Results from the redox capacity testing are summarised in 0. Results from all samples analysed were identical. From these results, the Warra subsoil at 180 cm depth can be classified as a 'suboxic' soil. Suboxic soils are defined as those that have a medium level of electron lability and who's 'reducing tendency is balanced against oxidising propensity' (Bartlett and James 1995). Nitrification is usually able to occur freely in these soils, indicating that the conversion of $NO_3^-$ to $NH_4^+$ would not have been favourable at the time sampling occurred.

**Table 4. Results of field redox testing from 1.75 to 1.8 m**

| Test | Result | Significance |
|---|---|---|
| Tetramethylbenzidine (TMB) oxidation | Positive | A positive result indicates a one-electron oxidation of TMB, usually by Mn oxides. |
| Chromium Oxidation | Negative | No oxidation of Cr(III) to Cr(VI) occurred but this can be inhibited by acidity. |
| Ferrous iron test | Negative | Conditions are not sufficiently reducing to allow reduced Fe to form.. |
| Easily reducible iron | Positive | Easily reducible iron is present, indicating some reducing potential |
| pH | 4.5 | Soil is acidic – reduced soils tend towards neutrality |
| Reduced Odour | Negative | Anaerobic decomposition is not occurring |

Waterlogged incubation

Results from the waterlogged incubation revealed that there was no measurable change in exchangeable-$NH_4^+$ concentration over the period of this experiment, although $NO_3^-$ concentrations did significantly decrease over time (0). Analysis of the $^{15}N$ enrichment of the exchangeable-$NH_4^+$ fraction revealed that an increase in enrichment occurred between the 0 and 25-day sampling periods, representing an average production of 0.1 mg $NH_4$-N/kg. A further decrease in enrichment was then observed between the 25 and 50-day periods, after which enrichment remained stable (0). The average amount of $NH_4^+$ produced after 75 days was equal to 0.06 mg-N/kg. There was no significant difference between the enrichment of samples with and without added Fe(II).

**Table 5. Average exchangeable-$NH_4^+$ and $NO_3^-$ concentrations (mg-N/kg), and atom % $^{15}N$ enrichment of the exchangeable-$NH_4^+$fraction in samples from the principle waterlogged incubation at 0, 25, 50 and 75 days.**

| Time (days) | Exchangeable $NH_4$ (mg-N/kg) | $NO_3$ (mg-N/kg) | Average Atom %$^{15}N$ Enrichment |
|---|---|---|---|
| 0 | 11.78 | $30.72^{C}$ | $0.3736^{A}$ |
| 25 | 11.49 | $24.14^{B}$ | $0.4173^{C}$ |
| 50 | 12.49 | $20.03^{AB}$ | $0.4030^{B}$ |
| 75 | 11.61 | $19.20^{A}$ | $0.3968^{B}$ |
| 75 Fe(II) | 11.57 | $16.41^{A}$ | $0.4005^{B}$ |

$^{A-G}$ Values with the same letter within columns are not significantly different (P>0.05).

Measurements of soil redox potential using the Bartlett test during this experiment found that the soil did not move from its original suboxic state. This result was confirmed by measurements obtained with the platinum reference electrode, which found samples to have an average *Eh* of 261 mV and 320 mV at the 50 and 75 day sampling periods.

The experiments conducted indicated that nitrate ammonification could be observed in the subsoil. However, the amount of $NH_4^+$ produced was small (0.06 mg-N/kg), and unless the rate of reduction was to increase over time it would be insufficient to account for all the $NH_4^+$ observed in the field. In addition, despite this soil being subjected to 75 days of low oxygen and waterlogged conditions it remained oxidising. These results indicate that reducing conditions that make the more rapid pathways of nitrate ammonification favourable i.e. either dissimilatory or abiotic nitrate ammonification, are unlikely to develop in this soil under periods of transient waterlogging.

Fixed ammonium

The concentrations of fixed $NH_4^+$ observed throughout the profile at Warra were low, and did not exceed 30 mg-N/kg (0). The absence of significant amounts of fixed $NH_4^+$ at Warra is not surprising given the mineralogy of the soil clay fraction. Smectite was the dominant mineral at all depths, with quartz, kaolin, and anatase also present. Kaolin (a 1:1 layer silicate mineral), quartz ($SiO_2$) and anatase ($TiO_2$) do not have structures capable of $NH_4^+$fixation. Smectite minerals, although they have a 2:1 structure, do not fix $NH_4^+$ readily, and soils dominated by smectite minerals are routinely observed to have fixed $NH_4^+$ concentrations less than 50 mg-N/kg (Black and Waring 1972; Feigin and Yaalon 1974). Because of the low concentrations of fixed $NH_4^+$ observed at the Warra site it is evident that the release of this fraction cannot be a major contributor to the concentrations of exchangeable-$NH_4^+$ observed.

**Average concentration (mg-N/kg) of fixed $NH_4^+$ on native vegetation and crop and pasture sites between 0-3.0 m. Figures in brackets are standard errors.**

| Depth (m) | Native Vegetation (mg-N/kg) | Crop (mg-N/kg) |
|---|---|---|
| 0-0.3 | 19.3 | 16.6 |
| 0.3-0.6 | 15.2 | 15.2 |
| 0.6-0.9 | 18.0 | 19.3 |
| 0.9-1.2 | 20.7 | 15.2 |
| 1.2-1.5 | 16.6 | 19.3 |
| 1.5-1.8 | 18.0 | 16.6 |
| 1.8-2.1 | 15.7 (0.7) | 20.1 (1.1) |
| 2.1-2.4 | 24.9 | 24.9 |
| 2.4-2.7 | 19.3 | 22.1 |
| 2.7-3.0 | 27.6 | 29.0 |

## Conclusion

The failure to observe the pathway of $NH_4^+$ formation is disappointing, and the reason for this is unknown. It is possible that the experiments conducted were unable to accurately reproduce the conditions present in the field needed for $NH_4^+$ formation. However, how experiments could have been modified is unknown. Any future studies need to be conducted in the field to ensure that the exact conditions necessary for $NH_4^+$ formation are achieved.

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