THE UNIVERSITY OF MANITOBA

NITROGEN MOVEMENT IN TWO MANITOBA SOILS

by

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ABSTRACT

The movement of nitrogen from calcium nitrate, urea and ammonium sulphate surface-applied at the rate of 500 lb N per acre was studied in two Manitoba soils. During the 1971 experimental period which lasted from June until October, the greatest movement occurred from $Ca(NO_3)_2$. There was some difference in the downward movement of nitrogen from urea and $(NH_4)_2SO_4$ depending upon the soil. The rate of oxidation of ammonium to nitrate was more rapid, and the depth of penetration of nitrogen greater in the Portage loam than in the Red River clay. Migration of ammonium from the point of application was limited in both soils.

The distribution of nitrogen in the Red River soil in spring and fall of the year following application showed an almost total disappearance of applied nitrogen from the $(NH_4)_2SO_4$ plot, and a partial disappearance from the urea and $Ca(NO_3)_2$ plots. There was some upward movement of nitrogen in the spring. However, by the fall sampling there was further downward movement of nitrogen into the soil profile. A similar study was not carried out on the Portage loam.

The chloride ion was applied to the soil surface at the rate of 500 lb Cl^- per acre to serve as a tracer of water movement. It was found, however, that the rate of chloride application was too low to serve this purpose since natural soil levels of chloride were very high.

Transport phenomena occurring during the freezing process

were investigated in column studies in the laboratory. There was evidence of a net transfer of moisture from the warmer to the colder regions of the columns. There was also an accumulation of nitrate at both the cold and warm ends of the soil columns. The use of NO_3^- as a tracer of liquid movement showed that moisture movement to the freezing zone occurred in both the liquid and vapour phases. There was also evidence of a return flow of condensed vapours to the warm end of the column.

Denitrification was found to take place in the soil columns. The rate was more rapid in the Portage soil than in the Red River soil, and was related to the initial moisture content. A more rapid denitrification rate occurred at the higher moisture content. The substitution of $Ca(NO_3)_2$ with $AgNO_3$ as a tracer resulted in a slower rate of denitrification, but there was also a difference in moisture and nitrate movement.

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INTRODUCTION

Movement of nitrogen in the soil is of considerable interest and has received somewhat extensive investigation. One reason for this is the important role that this movement plays in determining the availability of nitrogen for plant growth. Leaching may constitute one of the most important mechanisms of removal of nitrogen from the plant root zone other than crop absorption and possible denitrification and volatilization. Another reason is the increase in awareness of pollutants in the environment and the contribution from agricultural practices. It is already well known that the efficiency of nitrogen uptake by plants is relatively low (around 50%). A portion of the nitrogen which escapes uptake may move out of the soil-plant environment into drainage and ground waters where nitrate is the most prevalent form of nitrogen. Nitrate and nitrite nitrogen at high concentrations in water supplies may endanger the health of both man and animal. It has been well established that feed lots may, under certain conditions, contribute to ground water pollution, but little is known regarding the effect of nitrogen fertilization on the nitrate content of ground water.

The movement of fertilizer nitrogen is affected by a number of reactions which it may undergo in the soil system. The form in which it is added to the soil will therefore affect the way in which it is leached and the extent to which it is leached from the soil.

The objective of the first part of this investigation was to

compare the movement in the field of fertilizer nitrogen from three different carriers - calcium nitrate, urea and ammonium sulphate - applied at the rate of 500 lb N/acre. Two soil types representing some variation in reaction and texture were chosen for the experiment. Calcium chloride was also applied at the rate of 500 lb Cl^-/acre to allow comparison of the movement of Cl^- and NO_3^- in the soil. Nitrate and chloride are the ions usually considered most useful as indicators of water movement since they are generally not adsorbed by most soils and appear to move at equal rates with each other and with the water.

The second part of this investigation involved a laboratory study to examine some of the transport phenomena that accompany the freezing process in the soil. The convective and diffusive transport of nitrate has been fairly extensively studied by a number of workers. However, very little information is available on the transport of nitrate under non-isothermal conditions. Under natural conditions thermal gradients are always present in the upper layers of the soil. Such gradients are associated with moisture transfer within the soil profile. Thermally induced moisture translocation may significantly influence the net transfer of moisture and dissolved plant nutrients by changing the moisture content gradients within the soil profile. It was expected from the results of experiments done by other workers that the presence of an ice phase would greatly enhance the amount of moisture and salt transfer under a temperature gradient.

In Manitoba where farmland is subjected to severe cold

weather for almost five months of the year, soils freeze to a depth of approximately 4 to 5 feet each winter. Therefore column studies were carried out in the laboratory to examine water and nitrate transfer under a temperature gradient with the cold-side temperature below freezing.

LITERATURE REVIEW

FACTORS AFFECTING NITROGEN MOVEMENT

The mobility of nitrogen in the soil is a function of the chemical and physical properties of the soil and the climatic environment which actually prevails in the soil. Thomas (1970) in a review of the literature, listed some of the soil physical characteristics affecting the movement of nitrogen as pore-size heterogeneity, capillary conductivity, water content and the presence of a water table.

Pore-size heterogeneity

An aggregated soil has both intra-aggregate and inter-aggregate pore space. Coarse-textured, sandy soils, however, have little aggregation. In the most simple case, the solvent would move at a uniform rate through a porous medium composed of uniform particles that are inert to both solvent and solute. The solvent and solute would move at the same rate through pores of uniform size that are all completely filled. Under these conditions, if the solute were introduced across the column at a uniform depth, the concentration of the solute would be described by a normal distribution curve moving down the column. The curve would be symmetrical about the maximum concentration (or peak of the distribution curve) and would be found at the depth where the numbers of pore volumes was equal to solvent added after the introduction of the solute.

Under soil conditions this ideal simplified situation is rarely realized. Soil particles are neither uniform in size nor completely inert to water or dissolved salts. Furthermore, water from rainfall

or irrigation is not added continuously at a uniform rate. In all but single-grain structured soils there is a bimodal pore size distribution with the larger pores conducting most of the water at least in the upper part of the soil. Horton and Hawkins (1965) showed that the percolation of rainwater through the soil to the water table was accomplished throughout most of the flow path by downward displacement of water previously retained by the soil at field capacity. This is contrary to the formerly widely accepted belief that rainwater percolates to the water table primarily through pores which are not filled with water at field capacity. Even with abnormally large amounts of rain and with the soil at field capacity, most of the rainwater that infiltrates large pores flows to smaller pores by the time it has penetrated the large pores a few feet. The $D_2O-^{24}Na$ tracing of soil moisture movement by Haskell and Hawkins (1964) also demonstrated a downward displacement of soil moisture by infiltrating rain.

The miscible displacement studies of Biggar and Nielsen (1962) and Nielsen and Biggar (1961, 1962) suggest that movement of infiltrating water from larger to smaller pores may continue until it results in a downward displacement of soil moisture present in the soil at field capacity. A solution of a tracer ion flowing in the soil soon enters the smaller pores where almost stagnant water zones act as sinks to ionic diffusion. As a result, the diffusion of the tracer ion occurs from the larger pores having a high concentration into the smaller ones of lower concentration causing it to lag behind the water front. The concentration of ions not lost in the small pores moves through quickly with the water front. Values of ratio of hold-

back to water content have been measured to be three to four times
greater for unsaturated conditions than when the soil was saturated.
Desaturation of the soil eliminates larger flow channels and increases
the fraction of water within the soil which does not readily move.
The proportion of film water is significantly increased and the ion
distribution within the various-sized pores is modified according to
changes in film thickness and pore saturation. A soil which exhibits
greater holdback has a larger number of slowly conducting pores which
act as sinks for a tracer such as NO_3^- ion and a greater volume of
water must pass through the soil to reduce the NO_3^- ion to a low
concentration. Thus it is apparent that the distribution of an ion
some distance from its source depends upon the geometry of the porous
material in addition to the physical and chemical interaction of that
ion in solution and the media during flow.

Capillary conductivity

The capillary conductivity of a drying soil together with the
evaporative potential determines whether or not evaporation of water
will occur from a wet soil surface. When growing plants are present
on the land, both transpiration by plants and evaporation from soils
may operate as vapour sources. In this case the two sources supplement
each other in attempting to supply water rapidly enough to satisfy the
climatic potential. In the absence of plants, evaporation from the
land constitutes the sole vapour loss mechanism. In this case one of
the mechanisms by which the soil controls the rate of evaporation is
the limiting of the water supply to the evaporative site. Coarse-
textured soils generally have higher hydraulic conductivities at low

water suction (near saturation) than do fine-textured ones (Jackson,
1963; Willis,1960). The reverse is generally true at higher soil
water suctions and many soils have nearly identical capillary
conductivities at about 1 bar soil suction. Thus in coarse- as compared
to fine-textured soils, added water is transmitted downward more
rapidly when the soil is wet and upward more slowly as the surface
layers dry.

The effect of evaporation on solute movement is important in
soils in subhumid, semi-arid and arid regions. It is expected that
evaporation from bare soils would impede the rate of downward solute
movement. Cassel (1971) compared solute movement in covered and bare
plots, and found that soluble salts, in particular nitrate and chloride
ions, are leached to greater soil depths per unit of applied irrigation
water if water is applied under conditions of no evaporation.

A high evaporation rate, measured by the open pan method, is not
as likely to cause upward movement of solutes as is a lower evaporation
rate which permits the soil surface to remain wet. At high rates of
evaporation from bulk water, the rate of evaporation from the surface
of the soil exceeds the rate at which water could be conducted upward
at a gradient of matric suction low enough to keep the surface moist.
Accordingly the surface of the soil dries and the maximum rate of
evaporation is controlled by the rate at which water is conducted
through the soil to the surface. Flow through the dry layer is by
vapour diffusion, and the rate of such depends on the porosity of the
layer. According to Gardner (1958), the rate at which water can
be lost by vapour diffusion through a dry surface layer of soil is

usually less than 20 per cent of the maximum rate of loss by evaporation

from soil that is moist at the surface. The importance to nitrogen

movement lies in the fact that the barrier to upward water conduction

in the liquid phase also excludes the upward movement of nitrogen.

At low rates of evaporation from bulk water the rates of evaporation

from soil and from bulk water are approximately the same. The rate

of evaporation from the soil surface is controlled by the environmental

conditions that controlled the rate of evaporation from bulk water

and not by the properties of the soil. This is explained on the basis

that the conductivity of soils for water is great enough to keep

them moist to the surface at low rates of evaporation. Under these

conditions a great deal of solutes can accumulate at the soil surface.

Wetselaar (1961) showed that the effect of evaporation in moving

nitrate back towards the surface is important in the upper 30 cm (1 ft)

of soil. Chloride and nitrate applied to a tropical soil moved

downward following a rain but moved upward toward the soil surface

as the soil dried out. This upward movement was restricted to the

top 45 cm ($1\frac{1}{2}$ ft) of soil implying that any nitrate which has been

leached below this depth may not be recovered in the topsoil by

capillary movement. Thus upward movement of soil nitrate is retarded

if soil moisture is moved deeply enough into the soil profile.

Water content

The water content of a soil influences both the upward and the

downward diffusion or spreading of nitrogen. The data of Stewart and

Eck (1958) indicate that there is a downward spreading of surface-

applied nitrate nitrogen at all moisture levels from moisture equivalent

to the 15 atmosphere percentage. However, the amount and depth of
this spreading is definitely affected by the moisture content of the
soil. Downward diffusion decreases as the soil moisture content
decreases. The decrease in downward movement at low moisture
contents is attributed to a discontinuity of water films among
particles and an increase in tortuousity of the path (Porter et al.,
1960). Generally, downward movement of water is rather rapid in
the macropore systems of a medium- or coarse-textured soil. Because
of the generally lower water contents of well-drained sandy soils,
it is thought that a sandy soil would lose nutrients more easily
than a clay soil. However, there is some difficulty in correla-
ting the depth of nitrate movement with the soil texture. This is
mainly because at depths below the top 30 cm (12 ins) of soil, water
movement can occur at so many different water contents in the same
soil depending on the amount and frequency of application. Miller
et al. (1965) found that intermittent ponding of 5 cm (2 ins)
applications produced slightly more efficient leaching per inch
of water applied than did intermittent 15 cm (6 ins) ponding appli-
cations. Similar behaviour was also evident in flow in sandstone
columns studied by Corey et al. (1963). The difference in leaching
characteristics under the two methods of application was attributed
to the unsaturated flow conditions in the intermittent method combined
with the slower flow rate which allows more time for diffusion.
These studies predict that under field conditions rainfall would
provide a more efficient leaching than continuous ponding. However,
data by Gardner and Gardner (1969) indicate that the total water

lost by evaporation from soil would be nearly twice as much for the same time period for a water regime where three increments of 5 cm (2 ins) of water are applied compared with one increment of 15 cm (6 ins) of water. These contradictory results indicate that more research is necessary to relate water and solute movement for water regimes both in the presence and in the absence of evaporation from the soil surface.

Water table

A water table influences leaching through two opposite effects which may occur. A water table or pan which supports a temporary water table tends to promote the upward movement of water and nitrate during a dry period. However, since a high water table tends to keep the soil moist most of the time, a heavy rain causes water and nitrate to move down the larger pores without losing much in the aggregates. The fraction of intra-aggregate to inter-aggregate pore space is small under these conditions so that the holdback of nitrate by the soil is consequently small. Harmsen and Kolenbrander (1965) in a review of the research on soil inorganic nitrogen also discussed the influence of the water table on leaching. They observed that leaching was more rapid at high than at low water table. Where water tables are deep in the soil they have little or no influence on the upward movement of water. Under such conditions upward movement of moisture is not dependent on moisture being supplied by a free water table; the moisture now moves in the unsaturated state. Consequently water evaporated from a soil surface will be in part replaced by liquid movement from unsaturated layers below. This movement, though slow,

carries soluble ions with it as does liquid movement in the saturated state. In most cases the amount of mobile nitrogen in the subsoil is rather low and rising moisture brings little nitrogen to the topsoil. However, in some instances where soil conditions have favoured an accumulation of nitrate in subsoil layers (Wetselaar, 1960; Michalyna, 1959), the upward displacement of moisture can bring about an increase in nitrogen in the root zone of the soil.

TRANSPORT OF AMMONIUM NITROGEN

Ammonia and ammonium nitrogen occur in soils in three forms: the NH_4^+ ion, NH_3 gas or NH_4OH. The equilibrium between the three forms in solution depends on the solution pH. The form in which they are added to the soil has a marked effect on pH near the point of application. NH_3 or aqua NH_3 (NH_4OH) produces a very alkaline solution whereas $(NH_4)_2SO_4$ produces a slightly acidic one. In solution at pH 6 there is 1800 times as much NH_4^+ as NH_4OH plus NH_3, but at pH 8 there is only 18 times as much. Ammonia can be produced in the soil provided the pH is sufficiently high to induce the formation of ammonia. Calcium carbonate in the soil may result in a pH above 8 which is sufficiently high to induce the formation of ammonia from ammonium ions. The important point of this discussion is that NH_4^+ is relatively immobile in the soil whereas NH_4OH and NH_3 move much more freely.

Addition of fertilizer ammonium nitrogen to soils gives rise to ion-exchange reactions and microbiological reactions which affect its susceptibility to leaching. Ammonium nitrogen is held rather tightly by the exchange complex of soil clays and organic matter in an equilibrium with other ions in the soil solution. Ions in excess of

adsorption demands remain in solution and are free to move with the soil water. The movement of ammonium nitrogen is closely related to the movement of water. The magnitude of such movement, however, depends not only on water movement, but also on other soil characteristics. Ray et al. (1957) showed that the movement and retention of applied ammonium nitrogen in four Southern Minnesota soils were closely related to both the textures and cation exchange capacities of the respective soils. Movement is predominantly downward in the coarse-textured soil with a low cation exchange capacity whereas in the finer-textured soils movement was nearly equal in all directions and of much smaller magnitude. Nelson (1953) studied the movement of nitrate and ammonium nitrogen from ammonium nitrate in a virgin fine sandy loam soil under irrigation and found that ammonium nitrogen did not move more than 3 or 4 inches with the irrigation water. Various other investigators (Benson and Barnett,1939; Jackson and Chang,1947) have also reported the retention of ammonium nitrogen within a few inches of the point of application until nitrified.

Other factors which affect adsorption and therefore movement of ammonium nitrogen are the soil reaction and nature of the exchange material. Acid forest soils have a low ammonium fixation and retention capacity after addition of ammonium chloride (Overrein,1969). This is ascribed partly to the relatively high concentration of hydrogen ions and to a lesser extent to the presence of Al and Fe ions in the acid soil. Overrein's findings are in agreement with the observations on NH_4^+ fixation under acid soil conditions reported in another experiment (Barshad,1954).

Alkaline soils adsorb more nitrogen from ammonium sulphate than from ammonium hydroxide while the reverse is true for acid soils. Addition of ammonium sulphate to an alkaline soil decreases the pH, and this increases the fraction of nitrogen in the ammonium form. Since the diffusion coefficient of NH_4^+ in the soil is smaller than that of NH_4OH due to ion exchange reactions, the movement of ammonium away from the zone of application is restricted (Pang et al.,1973). Thus pH can affect the rate of diffusion of ammonium by modifying the ratio of NH_4^+ to NH_4OH. It can also affect the adsorption of NH_4^+ through its effect on the exchange capacity. The total cation exchange capacity of soil depends on the amount and kind of exchange material present. Soils which contain montmorillonite clay generally have a relatively high cation exchange capacity which is not pH-dependent. Those in which hydrous mica is the chief type of clay are intermediate, while kaolinitic soils have a low pH-dependent cation exchange capacity. However, the capacity of a kaolinitic soil rich in humus may exceed that of a montmorillonitic soil containing an equal amount of clay, but poor in humus. In such a soil rich in humus, addition of $(NH_4)_2SO_4$ can cause a reduction in cation exchange capacity through the production of H^+. This decrease in the adsorption capacity of the soil results in increased mobility of NH_4^+.

The ammonium ion is subject to nitrification, which is important to the movement of nitrogen when applied in the ammonium form. When nitrate or nitrite is produced the convection or diffusion of these ions takes place readily. The rate at which nitrification takes place depends on the fertilizer concentration. Tyler et al. (1958) showed

that the greater over-all lateral and vertical diffusion of ammonium nitrogen in coarser textured soils reduced the NH_4^+-N concentration and allowed nitrification to proceed more rapidly following application. The results of work done by Pang et al. (1973) support these findings. They found that the magnitude of NO_3^- or NO_2^- production from band-applied NH_4^+-type fertilizers was dependent upon the concentration. Soil characteristics can restrict movement of ammonium away from the zone of application and cause a retardation of the transformation process. Unless nitrification occurs to transform some of the applied nitrogen to a more mobile form it does not become well distributed in the soil.

TRANSPORT OF UREA NITROGEN

The movement of urea like that of ammonium nitrogen is complicated by the number of possible reactions which it can undergo in the soil.

Urea is readily soluble in water, and the dissolved urea is hydrolysed to ammonium carbonate by soil bacteria and enzymes. Chin and Kroontje (1963) have demonstrated the rapid hydrolysis of urea. This rate varies between soils, but is temperature-dependent in a particular soil. It is also dependent on the nature and condition of the soil, level of application, and probably other factors. Gasser (1959) and Ernst and Massey (1960) have shown that following hydrolysis, loss of nitrogen by volatilization is often significant. The nitrification reaction following hydrolysis of urea to ammonium carbonate, though less rapid, proceeds readily and closely resembles the conversion of other ammonium carriers to nitrate.

Experiments have shown that urea can be moved through soil columns but it is much less subject to leaching than is nitrate (Broadbent et

al.,1958; Conrad and Adams,1940). This is believed to be due to retention of urea by weak adsorption forces, hydrolysis to ammonia which is then held as an exchangeable cation or to a combination of the two. It is possible to demonstrate the fact that urea is held by weak adsorption forces by elution analysis. Broadbent et al. (1958) showed that nitrate was eluted first and had a higher narrower peak than urea. The separation between peaks was much better in a clay than in a sandy loam.

Chin and Kroontje (1963) have attributed urea retention in soils to processes involving the formation of relatively stable, non-leachable complexes between urea (or nitrogen compounds produced during urea hydrolysis) and organic matter. They also noted that differences between soil types with respect to urea adsorption were primarily related to organic matter content. Further support for this theory is provided by work done by Overrein (1968). He investigated the effects of urea application rate on losses of nitrogen by leaching in an acid forest soil profile. The accumulated losses of nitrogen were slight or even negative at urea application rates less than 250 kg urea N/ha. At these rates a greater proportion of the added N was retained by the raw humus layer. Evidence of a saturation point with respect to the over-all urea retention in the raw humus was provided by a marked switch from negative to highly positive leaching losses at application rates exceeding 250 kg N/ha. In another study, Overrein (1969) compared the leachability of urea, ammonium and nitrate nitrogen in an acid forest soil. He found that nitrogen added as ammonium chloride occupied a position intermediate between nitrate and urea in its susceptibility to leaching. Cole and Gessel (1965) working with moder-

ately acid forest soils, found that 88 per cent of nitrogen added as ammonium sulphate passed through the forest floor during a period of heavy rainfall, whereas the corresponding figure for the urea application was 65 per cent.

In short-term leaching experiments on acid and alkaline California soils, Broadbent et al. (1958) found that urea N occupied a position intermediate between nitrate and ammonium N in its susceptibility to leaching. To account for the difference in their work as compared to that of Overrein (1968,1969), great emphasis was placed on the humus layer. Without a doubt great differences exist between nitrogen movement out of the humus and nitrogen movement within the underlying soil portion. The experimental work of Broadbent et al. (1958) is based on soils not directly comparable to the highly acid podzolic forest soil used in Overrein's lysimeter investigation – neither physically, chemically nor biochemically.

In most agricultural soils where hydrolysis is very rapid, the movement of surface-applied urea nitrogen is believed to be of little practical importance and generally should be considered relatively immobile like ammonium nitrogen.

TRANSPORT OF NITRATE NITROGEN

For cropped agricultural land it is generally accepted that the drainage nitrogen losses from the soil consist primarily of nitrate. Nitrate nitrogen is considered mobile in the soil water since it is only weakly adsorbed by some soils and not at all by others. It is generally assumed that NO_3^- moves at the same rate as water and that adsorption is not a major consideration (Pratt et al.,1972; Stewart,

1970). However, in soils high in amorphous inorganic material, positive adsorption occurs. Kinjo and Pratt (1971) demonstrated NO_3^- adsorption in some acid soils of Mexico and South America. The magnitude of this adsorption depended on the NO_3^- concentration and the pH of the electrolyte solution. Soils in temperate regions contain predominantly 2:1 type layer silicate clay minerals and in such soils NO_3^- is not adsorbed. Instead NO_3^- is repelled by the negatively charged soil particles giving the effect of a negative adsorption.

Results of a laboratory study carried out by Thomas and Swoboda (1970) suggest that anion exclusion plays an important part in increasing the movement of salt through soils with high cation-exchange capacities. It is not suggested that their work adequately describes leaching under field conditions. There are other factors of equal or greater importance than anion exclusion in determining the rate of salt movement through soils. However, the conclusions made by Thomas and Swoboda (1970) from their laboratory study fit field observations of efficient leaching on the same soils. Dyer (1965a,b) has also shown a quantitative relationship between the depth of anion leaching and the quantity of soil water which does not hold anions. The larger the anion exclusion volume, the deeper salts will be leached at a given soil water content and application. The anion exclusion effects become more intense at lower moisture levels, indicating that Cl^- and NO_3^- ions are not perfect tracers of all the moisture contained in unsaturated soils.

The importance of nitrate in leaching losses of nitrogen is generally undisputed. However there is much conflict of opinion over the

magnitude of such losses. The effects of cropping, climate, management
and soil conditions are reflected in the various figures reported.

Allison (1965) concluded that leaching of NO_3-N would be of
little significance in dryland farming where the soil was frozen
during winter months. In the prairie provinces most of the improved
agricultural land is either seeded to annual crops, or is in summer-
fallow in preparation for annual crops of the following year. Fallowing
can affect the level of available soil nitrogen. A knowledge of the
fate of such nitrogen is very important in deciding whether, and if so
to what extent fallowing contributes to the nitrate nitrogen found
in streams and lakes. Nitrate nitrogen is produced mainly in the
surface six inches where fresh organic matter is being added regularly.
The amount of nitrate nitrogen that accumulates during fallowing
varies depending on the soil characteristics and organic matter
content. The values usually range from 40 to 100 pounds of nitrogen
per acre to a depth of 2 feet (Ridley and Hedlin,1967; Hedlin,1970;
Paul,1972). Frequently though, nitrate produced at the surface may
be leached beyond the four foot depth which is the maximum depth for
appreciable root activity of most spring grains (Michalyna,1959; Staple
and Lehane,1952). Summerfallowing can be justified in regions where
soil water deficit is the only factor that restricts plant growth and
irrigation is not feasible. In such semi-arid regions, nitrate leached
downward with percolating water may be brought back by evaporating
water (Miller,1906; Krantz et al.,1943), though generally, this is
not reported.

In Southwestern Saskatchewan Doughty et al. (1954) measured

NO_3-N accumulations of 100 to 400 pounds per acre below the root zone (4 feet) in soils cultivated 12 to 14 years in a spring-wheat-fallow sequence. No accumulation of NO_3-N was found in grasslands. Bolton and his co-workers (1970) too, demonstrated that the amount of movement varies with the kind of vegetation growing on the land. They studied the nitrogen content of water in tile drains placed at a depth of six feet as affected by fertilizer application and cropping system over a 7 year period. The average concentration of nutrients in effluent from the tile drains reflected the effect of cropping system and fertilizer application. The amount of nitrogen lost from corn plots without any commercial fertilizer was approximately 10 times that lost from fertilized bluegrass plots. Leaching of NO_3-N can occur on soils in corn or similar row crops having a relatively low water requirement during May and June, the months of highest precipitation (Power, 1970).

Cunningham and Cooke (1958) followed the changes occuring in levels of NH_4^+-N and NO_3-N in a heavy soil at Rothamsted, which was either kept bare or sown with ryegrass with and without the addition of nitrogen fertilizers. They found that only persistent and heavy rainfall (which caused drainage through 20 inches of soil) could reduce high levels of nitrate in the surface soil. However, whereas the decrease in the surface soil nitrate levels was accompanied by an increase in subsoil nitrate levels in the fertilized plots, there was no corresponding increase in the unfertilized plots. They estimated that the losses of nitrogen from the cropped soil which were not accounted for by uptake by grass probably did not exceed one-tenth of the quantity

applied. On a light soil, nitrate is leached more easily and possibly removed from the root range of crops by rainfall (Webster and Gasser, 1959).

Field trials using isotopic nitrogen indicate that the degree of crop recovery of applied nitrogen ranges from 30 to 45 per cent during the first year in Manitoba (Cho, 1968). However, because of the low rates of application relative to crop removal, nitrate pollution of water reservoirs in prairie provinces due to application of chemical fertilizer seems unlikely. Low crop recovery was also reported by Wagner (1956) whose data also suggested extensive leaching. Samples of internal drainage waters collected periodically during four years indicated a significant amount of nitrate nitrogen leached through the subsoil. Recovery by the crop averaged only about 35 per cent of the amount applied, suggesting that liberal fertilization may lead to leaching of large amounts of nitrate from a soil, and its possible movement into underground aquifers. A similar opinion was expressed by Johnston et al. (1965) who found high percentages of applied nitrogen in tile drainage effluent under different cropping programs. There were sufficient nutrients in the effluent to possibly cause significant growth of algae in the downstream ditches.

It has been shown that the presence of nitrate in tile drains does not necessarily mean that the nitrate will eventually find its way to water reservoirs. In field studies at Brawley, California, Meek and his co-workers (1969) found that nitrate from heavily fertilized plots disappeared as the soil solution approached the water table which was approximately 6 feet deep. On the other hand, some deep wells in California ranging from 760 feet to 1254 feet

contained approximately 1 ppm in 1950, 17 to 30 ppm in 1959 and 10
to 17 ppm NO_3-N in 1962 (Broadbent,1971). There is no full explanation
of why in one case nitrate disappeared when it reached the groundwater
and did not disappear in the other case although this nitrate stability
can be accounted for by the lack of energy for denitrifying organisms.
Meek et al. (1969) correlated their nitrate concentration decrease and
its eventual disappearance with a decrease in the redox potential.
Thus, denitrification was proposed as a pathway for loss of nitrate
in the field. It is therefore desirable to promote denitrification
when it occurs below the root zone in order to reduce nitrate contami-
nation of groundwater. It is possible to increase denitrification
before the soil water enters the tile line (Meek et al.,1970). This
may be accomplished by submerging the tile lines, thus causing the
soil solution to flow through a zone of saturated soil where conditions
would be more favourable for reduction. The denitrification rate
in such a submerged zone would depend to a large extent on the nitrate
and dissolved oxygen concentrations and on the quantity of soluble
carbon carried down in the soil solution to the submerged zone.
Meek et al. (1970) also demonstrated that periodic drying increased
soluble carbon in the soil solution, which would tend to promote
denitrification.

THEORY OF MOVEMENT OF NITROGEN IN SOIL

Nitrogen dissolved in the soil solution can move by molecular
or ionic diffusion due to concentration gradients within the solution,
or by convection due to mass flow of the soil solution. The processes
of diffusion and convection can occur simultaneously, either in the

same direction or in opposition. Factors which determine the extent
and direction of N movement by convection are 1) the concentration
of nitrogen in the soil solution, 2) the direction and rate of movement
of the soil solution, 3) the soil texture and cation exchange capacity,
4) the degree of interaction between nitrogen in the soil solution and
the soil constituents, 5) the rate of transformation of nitrogen into
various forms.

Diffusion

Diffusion in soils can occur only in that fraction of the soil
which is filled with water (or air in the case of vapour diffusion).
For diffusion through the soil water, Fick's first law of diffusion
may be written:

$$J = -D\theta \frac{dC}{dx} \qquad (1)$$

where J is the flux of the diffusing substance per unit area of soil,
D the effective diffusion coefficient, θ the water content on a
volume basis, C the concentration of the diffusing substance in the
soil water and x the space variable. Because of tortuousity and the
effect of adsorbed water, D in the soil is generally less than in bulk
water. In the case of a saturated soil, θ is equal to the porosity.
The diffusion coefficient decreases with decreasing wetness θ, so
that J is strongly dependent upon the degree of unsaturation. This
is borne out by the data of Porter et al. (1960) and Klute and Letey
(1958). D is also dependent upon temperature and to some extent
upon concentration. To preserve electrical neutrality, the diffusion
of any ion must be accompanied by the diffusion of some other ion or
ions. The effective diffusion coefficient for a combination of ions

is some average of the separate coefficients for the different ionic species.

The constitutive relation, or force-flux relation as expressed by Fick's first law should be combined with the equation of continuity to describe diffusive transport in soil (one dimensional form). The resulting second order equation or Fick's second law of diffusion is

or

$$\frac{\partial M}{\partial t} = D\theta \frac{\partial^2 C}{\partial x^2} \qquad (2)$$

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \qquad (3)$$

where M is the quantity of substance per unit volume of soil and t is time. The physical meaning of equation (3) is that the rate of increase in concentration of a substance within a fixed volume is due only to the net influx of the substance transported by the concentration gradient. There are many solutions of equation (3) depending upon the boundary conditions.

Diffusion and chemical reaction

If nitrogen is adsorbed or produced in the soil according to an essentially irreversible reaction, a term expressing the time rate of reaction is added to the diffusion equation. Equation (3) may then be written

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} \right) + Q \qquad (4)$$

where Q is the volumetric reaction rate which may be a function of position, concentration or time. A form of equation (4) is generally used in soil science to describe nitrogen transport with production or denitrification. Q is commonly chosen to be a linear function of C (Cho,1971). This choice makes the resultant equation linear and

the analytical solution easily found.

If the reaction rate is proportional to the concentration, then

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \pm kC \qquad (5)$$

where k is the reaction rate constant and $\pm$ refers to either production or disappearance. Substitution of $C = C^* e^{\pm kt}$ into equation (5) results in the following equation:

$$\frac{\partial C^*}{\partial t} = D \frac{\partial^2 C^*}{\partial x^2} \qquad (6)$$

which is identical in form with equation (3). Thus the solution of equation (5) is generally $e^{\pm kt}$ times greater or less than the solution of equation (3). The above analysis indicates that the diffusive transport of a species such as NO_3^- in soil may be greatly altered depending upon the presence or absence of chemical reaction.

Diffusion and convection

If the soil solution itself is flowing within the soil, then nitrogen dissolved in the solution will be carried along with it. Neglecting "salt sieving" and other interaction effects (Kemper, 1960), the flux of nitrogen due to water movement is simply

$$J = qC \qquad (7)$$

where q is the flux of water in the x direction (i.e. the volume of water crossing unit area in unit time). This flux can be related to the average velocity of water in the soil, v, by the expression $q = v\theta$. The rate of change of nitrogen content of the soil per unit volume of soil due to convection is then written

$$\frac{\partial M}{\partial t} = -\frac{\partial J}{\partial x} = -\frac{\partial (qC)}{\partial x} \qquad (8)$$

Both q and C may be functions of x .

When diffusion and convection take place simultaneously, equations (3) and (8) are combined to give

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2}\right) - \left(\frac{\partial v C}{\partial x}\right) \qquad (9)$$

The process of diffusion plus convection is more complicated than is indicated by equation (9). This arises from the fact that the actual velocity of water flowing in pores is not uniform. The velocity near the centre of a pore's cross section exceeds that near the edge, and the velocity in wide pores exceeds that in narrow or constricted or lateral pores. The result of this variation in pore velocities is a mixing process known as hydrodynamic dispersion. This dispersion process can enhance the diffusion process, and at sufficiently high velocities it may completely obscure it. The effective diffusion coefficient of equation (9) depends upon flow velocity and tends to increase with increasing flux (Nielsen and Biggar, 1963; Taylor, 1953; Scheidegger, 1963). It is therefore generally called the dispersion rather than the diffusion coefficient.

Substitution of t with η and $(x - vt)$ with X converts equation (9) into

$$\frac{\partial C}{\partial \eta} = D \frac{\partial^2 C}{\partial X^2} \qquad (10)$$

Equation (10) is identical in form with equation (3). Thus the $(x - vt)$ or X variable behaves like x of equation (3). In other words, the moving coordinate for a convective system can be described in a way identical to the stationary coordinate in a diffusive system. The straightforward physical interpretation is that a substance is transported by a moving fluid with the diffusive transport process taking place within the moving fluid.

Diffusion plus convection and chemical reaction

In practical situations, both diffusion and convection may account for the net effect of transport of nitrogen in the soil. Also, reactions such as mineralization, immobilization, oxidation and denitrification will undoubtedly occur. A transport equation for one nitrogen species may be written as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \frac{\partial (vC)}{\partial x} + Q \qquad (11)$$

In order for equation (11) to be applicable to a system, a functional relation of Q should be known. Transport of ammonium with oxidation under the assumption that Q is a linear function of the concentration was treated by Cho (1971). An interesting feature of the solution is that the separate distribution of NH_4^+, NO_2^- and NO_3^- throughout the soil column is time dependent.

If the volumetric reaction rate, Q, represents a reversible reaction such as the exchange reaction of NH_4^+, the form of equation (11) becomes much more complicated. Lapidus and Amundson (1952) and Oddson et al. (1970) have presented some simplified solutions of equation (11) with reversible reaction and finite rate. However, in many practical cases the local equilibrium assumption seems justified. Many results of ion transport through ion-exchange materials were satisfactorily explained by this assumption (Hashimoto et al.,1964). According to this assumption, Q is a function of $\frac{\partial C}{\partial t}$ so that equation (11) can be simplified greatly. If Q is a linear function of $\frac{\partial C}{\partial t}$ such as $K \frac{\partial C}{\partial t}$, then the term, $1 + K$, becomes a very important factor which governs the modification of diffusive as well as convective transport of an exchangeable ion. For instance, the

diffusion coefficient is reduced from D to $D/1+K$ and the average

speed of the ion due to convective transport is reduced from ν to $\nu/1+K$

The physical meaning of this modification can be stated as follows:

if there is a reversible reaction, the net effect of both diffusive and

convective transport is reduced by a fraction equal to the fraction

of ion in solution which is subject to diffusive and convective influences.

MOISTURE AND SALT MOVEMENT UNDER A THERMAL GRADIENT

Soils under natural field conditions are subjected to continuous

seasonal and diurnal temperature fluctuations which produce thermal

gradients. Seasonal fluctuations affect soil temperatures to depths

greater than the rooting zones of most crops while diurnal ones

influence approximately the surface 30 cm of bare soil (Smith, 1932).

When temperature gradients are present in a system water moves from the

region of high to a region of low temperature (Bouyoucos, 1915).

One of the most striking soil moisture flow phenomena which

develops concurrently with a significant thermal gradient occurs during

the winter months. Temperature conditions during the winter tend to

cause water to move upwards both in the vapour and in the liquid

phases. In the summer, on the other hand, temperature conditions

tend to cause downward movement of soil water in both liquid and

vapour phases (Edlefsen and Bodman, 1941).

Lebedeff (1927) conducted a field experiment over the winter

months in Russia and concluded that more than 6 cm of soil water moved

upward into the soil profile in response to the seasonal thermal

gradients. This upward movement can cause a significant lowering of

the water table. Willis et al. (1961, 1964) observed a drop in the

water table of more than 1 m during the winter. This tendency is
reported to become more pronounced as the soil moisture content increases
from the wilting percentage towards the 1/3 atmosphere moisture percentage.
Overwinter studies (Benz et al.,1968; Willis et al.,1961,1964) showed
that the drop in water table levels is associated with depth of frost.
Increased depth of the water table during the freezing period was
accompanied by increased soil moisture in the surface 3 feet.

The thermally induced moisture flow may significantly affect
the net transfer of the soil water and nutrients by changing the
moisture content gradients and the capillary conductivity, in addition
to the direct effects of mass transfer. Campbell et al. (1970)
demonstrated moisture and nitrate redistribution in a closed system
experiment with soil cylinders placed in holes in the field after
freeze-up. Since at the prevailing soil temperatures nitrification
would be minimal and denitrification unlikely, they thought that
the redistribution of nitrate must have resulted from liquid flow.
Both nitrate and moisture tended to accumulate near the surface in the
winter but the reverse in the soil temperature gradient in the spring
caused a return to an approximately uniform distribution of both
nitrate and moisture in the soil profile. These changes (winter and
spring) were much less marked when the initial moisture content was
near the wilting percentage.

Laboratory studies have also shown a net transfer of moisture
from warm to cold regions which was induced by the imposed thermal
conditions (Gurr et al.,1952; Taylor and Cavazza,1954; Hutcheon,1958;
Weeks et al.,1968). Various hypotheses have been advanced for the

mechanism of thermal moisture transport. Water is assumed to move
in both the vapour and liquid phases in response to both soil-water
pressure and thermal gradients. It has been shown (Thomas, 1921)
that provided the temperature is held constant, the vapour pressure
of soil moisture varies only slightly under soil moisture conditions
above the permanent wilting percentage. It does, however, change
markedly with temperature. Vapour tends to move from positions of
higher to those of lower vapour pressure, whereas liquid at constant
soil moisture content tends to flow from points of lower surface
tension to those of higher surface tension. An increase in soil
temperature with distance below the soil surface produces for a
given soil moisture content an accompanying increase in vapour pressure,
that is to say, a negative vapour pressure gradient. For a given
moisture content, an increase in soil temperature with increasing
depth has, however, an opposite effect on the surface tension of soil
water in that the surface tension decreases with depth. Therefore
liquid in the unsaturated soil could flow from warm to cool regions
under the influence of a surface tension gradient.

Bouyoucos (1915) found that when a soil column was divided into
two parts by an air space across which the temperature gradient was
applied, much smaller quantities were transferred than in a continuous
column. He concluded that the flow must take place largely in the
liquid phase and gave a qualitative explanation of the flow being caused
by a change in the water affinity of the soil with temperature. However,
on the grounds that the effect of temperature on the surface tension of
water is not great enough to cause the observed water transfer, Richards

and Weaver (1944) and Smith (1940) suggested that vapour convection would be a more important mechanism than liquid movement. Like Bouyoucos (1915), Taylor and Cavazza (1954) attempted to segregate liquid and vapour flow. They compared the thermal distribution of moisture in continuous and segmented columns at similar initial moisture contents. The segmented columns were prepared in five sections isolated by narrow air gaps. Their conclusion was that the flow of moisture from warm to cool regions occurs largely in the vapour phase. The condensation of excess vapours in the cooler regions results in a flow of moisture in the liquid phase from cold to warm regions once a favourable pressure gradient within the liquid has been established. When the soil is sufficiently moist to permit active liquid flow, a state of equilibrium cannot be reached and a continuous circulation of water takes place within the enclosed column.

Gurr et al. (1952) assessed the contribution of liquid and vapour flow to the temperature effect by measuring the changes in the distribution of a small amount of soluble salt in the soil. It was assumed that the movement of soluble salts was due to transport in the liquid phase only. They found a transfer of chlorides toward the warmer end of the column, indicating that liquid carrying salts in solution had been transferred in the direction of increasing temperature. However, there was a net transfer of water in the opposite direction which they attributed to vapour flow in the direction of hot to cold and of greater magnitude than either of the two liquid water components during transient periods of the experiment. Weeks and his co-workers (1968) also used the chloride ion as a tracer to distinguish between

liquid and vapour movement, and obtained results similar to those of
Gurr et al. (1952). In addition, they measured suction head values
with tensiometers located at three positions along a horizontal column.
Liquid water transfer toward the warm end was assumed to be due to an
induced suction head gradient and generally exceeded thermally induced
liquid flow in magnitude in both the transient and steady state periods.
The increase in soil moisture suction as the temperature drops should
cause an initial liquid moisture flow from warm to cool. The following
discussion of the mechanism is that proposed by Gurr et al. (1952).
They assumed that the rates of flow of liquid and vapour in horizontal
columns were proportional to the pressure gradients in the liquid and
vapour respectively.

In an unsaturated soil, water is at a hydrostatic pressure P
which is negative with respect to that at a free flat water surface,
and is given (Edlefsen and Anderson, 1943) by

$$P = \frac{2S}{r} \qquad (12)$$

where S is surface tension and r, radius of curvature of the liquid
surface in the soil pores. Since S decreases with increasing
temperature, and r is assumed to have a constant negative value, P will
increase with increasing temperature. Consequently a temperature
gradient established in a uniform soil of uniform water content will
result in a pressure gradient which will tend to move liquid water in
the direction of decreasing temperature. There will also be a similar
tendency for water vapour to flow in the same direction since it may
be assumed that the vapour pressure of the soil water, p, will increase
with temperature as in the case of the vapour pressure of free water p_o.

Although water will at first move in the direction of decreasing

temperature in both the liquid and vapour phases, it has been shown that

this condition of flow may be only temporary. The temperature induced

pressure gradient within the liquid phase is extremely small. At the

end of what Gurr et al. (1952) termed a first stage in the adjustment of

water to a temperature gradient, sufficient movement will have taken

place to remove the gradient in P in the liquid phase. If as it was

assumed by Gurr et al. (1952), there is no effect from soluble salts, the

relation of p to T at this stage may be considered through the equation

or
$$P = \varrho RT \log \frac{p}{p_o} \qquad (13)$$

$$\log p = \log p_o + \frac{P}{\varrho RT} \qquad (14)$$

where T is absolute temperature, R the gas constant per gram of water,

and ϱ the density of water.

Any increase in T will cause an increase in p_o, and with P constant

and negligible changes in ϱ disregarded, $\frac{P}{\varrho RT}$ will become a smaller

negative quantity. Hence, according to equation (14), p will increase

with temperature and there will be a tendency for vapour to flow

even when the water in the system is so adjusted that there is no

longer a tendency for liquid to do so. The movement of vapour in the

direction of decreasing temperature can continue further until as a

result of evaporation and condensation, a condition of vapour pressure

equilibrium is reached. The relation of P to T can then be examined

by means of equation (13) in which p is now taken as constant. Since

p_o increases with T and $\log \frac{p}{p_o}$ is negative, it follows that P will

decrease with increasing values of T. Hence liquid will tend to

flow in the direction of increasing temperature – a direction which

is the reverse of that during the first stage of adjustment (Gurr et al.,1952).

Gains or losses of water affect the vapour pressure of soil water only slightly in a moist soil at constant temperature. Consequently, in a soil that is sufficiently moist to provide a connected conducting path for liquid water, the reversal in direction of liquid flow will probably begin before the vapour pressure gradient and the rate of flow of vapour have decreased appreciably, thus preventing a condition of vapour pressure equilibrium. A circulating system will therefore operate in which vapour moves in the direction of decreasing temperature and liquid moves in the opposite direction as far as permitted by the presence of conducting water films. Within the closed system, flow in each direction will finally become equal and will be governed by the pressure gradients and the permeability for the liquid and vapour phases respectively.

Moisture transfer under temperature gradients is negligibly small both in very dry and in very wet media, but attains a fairly well-defined maximum at an intermediate moisture content which appears to depend on the soil-water tension and on the air-filled pore space (Hutcheon,1958; Gurr et al.,1952). Compared to the flux arising from head gradients, this thermal flow becomes relatively more important as the hydraulic conductivity decreases (Cary,1965, 1966). In unsaturated soils the relative importance of thermally induced flow rises rapidly as the moisture content decreases. The decrease in moisture content is accompanied by a decrease in the thermal liquid moisture flow and by an increase in the thermal vapour

moisture flow.

The process of moisture movement in a porous medium is considerably altered by the presence of an ice phase (Dirksen and Miller, 1966). Frost action creates a pressure gradient within the liquid phase from warmer to colder regions, and this inhibits any tendency for liquid to flow from colder to warmer regions of the soil columns (Hutcheon, 1958). Hutcheon also found that frost-induced pressure gradients within the liquid phase will not cause any appreciable flow of water when soil moisture conditions are drier than those characteristic of moisture tensions in the vicinity of one atmosphere. Hoekstra (1966) made some general observations on moisture flow from unsaturated unfrozen soil to a freezing interface. He noted that the time at which the water content at a certain location in the sample starts to increase nearly coincides with the time of freezing at that location. Thus, as soon as ice formation takes place at a certain location, the water content at that location starts to increase. Moisture content profiles showed that the water content in the unfrozen soil decreased sharply toward the frozen soil. The points of lowest water content in the moisture distribution profile marked the boundary between frozen and unfrozen soil. Hoekstra (1966) also discussed the forces that drive the water into the frozen soil. In an unfrozen soil the chemical potential is a strong function of moisture content, and decreases with decreasing moisture content, so that if a temperature gradient is placed across a soil column and the temperature of the cold plate is higher than the freezing temperature, an equilibrium moisture content distribution will be reached. On the

other hand, in a frozen soil the chemical potential is independent of the total water content present; i.e. the chemical potential of ice is unaffected by the presence of soil. Also the amount of ice can increase without affecting the amount of unfrozen water. No equilibrium moisture content is reached, so the frozen soil tends to act like a sink. With the first appearance of ice, the frozen soil actively extracts water from the unfrozen soil, supposedly due to attenuation of the liquid water films associated with ice surfaces. The resultant water content gradient in the unfrozen soil induces hydraulic flow toward the frozen soil. Dirksen and Miller (1966) suggested that during the early stages of their experiment thermal transport in the unfrozen soil was inconsequential compared with this hydraulic flow. Later as the rate of ice accumulation diminished and the hydraulic gradient was dissipated, thermal water transport became relatively more important.

As water moves from warmer to cooler areas, the ice crystals in the cooler areas grow as the arriving water freezes out. This may continue until ice crystals fill the pore spaces. At this stage the continuous liquid films along the soil particles are pushed apart by the continued ice crystal growth. This is the beginning of an ice lens that leads to frost heave. Although water may still move from warmer areas to these large ice lenses, little water can move past them so the lenses continue to grow. Hoekstra (1969) showed that these ice lenses in an unsaturated soil form at a considerable distance behind the freezing front.

Though freezing may impede percolation, causing a build-up of water in the frozen zone, water may still infiltrate and percolate

through frozen soil. Post and Dreibelbis (1942) defined three types of frost which are determining factors in regard to the transmission of liquid through frozen soils. 'Concrete' frost structure is characterized by small ice crystals in a very dense complex. This type of frost is impermeable when it occurs on bare agricultural soils. 'Honeycomb' type has a loose porous structure and is associated with shallow freezing early in the winter along with a high degree of aggregation such as is found under grassy vegetation and in soils of high organic matter. It is more permeable than unfrozen soil. 'Stalactite' frost structure is characterized by many small icicles connecting the heaved surface to the soil below. This type is formed after the rapid freezing of partially thawed honeycomb structure.

Where a more permeable frost is formed, some soil water migration takes place in the frozen soil. Liquid films of varying thicknesses remain in the soil particle-ice interfaces and in the soil particle-air interfaces. These films may contain very high concentrations of soluble salts. Cary and Mayland (1972) showed that both water and salt will move from warmer to cooler areas in unsaturated frozen soil. Their results suggested that mass flow of dissolved salts in a liquid film of water was the principal transfer mechanism even though vapour and salt diffusion were sometimes significant.

These results differ from those cited previously which showed an accumulation of chloride in the warm side, and no net movement in the liquid phase from the hot to the cold plate (Gurr et al., 1952; Weeks et al., 1968). In frozen soil, however, liquid movement from warmer to cooler areas becomes significant. Hoekstra (1966, 1969)

attempted to resolve this anomaly on the basis of the difference in the properties of adsorbed films of water in unsaturated soil. The physical adsorption forces in the water films in unfrozen soil are nearly independent of temperature (Philip and de Vries, 1957). If the properties of adsorbed films in unsaturated soils do not change with temperature, no liquid transfer in unfrozen soils can be expected. However, in frozen soil the unfrozen adsorbed water films reduce their thickness with decreasing temperature below 0C as more adsorbed water goes into the ice phase. As a result, water movement in the liquid phase occurs in the direction of decreasing film thickness, that is to the cold side. Most of the flow in the unfrozen soil is not a direct consequence of the temperature gradient in the unfrozen soil, but is mainly a consequence of events taking place in the frozen part of the column which creates a hydraulic gradient in the unfrozen soil. Hutcheon (1968) suggested that some vapour movement occurs to the cold plate. Where flow is not inhibited by freezing conditions which retain all the condensed vapours as ice, there is some liquid flow from the freezing front to a short depth below. Even when this cold circulation system is inhibited during the early stages of redistribution of moisture, there is still a warm circulation system operating, induced by the net evaporation within the warmest segments of the column. That is, there is a return flow of liquid from adjacent regions into the evaporation sink. During the course of the experiment, as the moisture content decreases and therefore permeability decreases, the frost-induced liquid flow to colder segments of the column is

restricted. The influence of evaporation on liquid flow then becomes more apparent. When ice ceases to form and a steady state has been attained, the temperature gradient is responsible for any further movement of water in the unfrozen soil. In a closed system this involves a circulatory flow with water moving toward the cold end in the vapour phase, and a counter current toward the warm end in the liquid phase.

The ability of a thermal gradient to indirectly cause the transfer of significant amounts of soluble salts from cool soil regions into warmer regions has been demonstrated (Gurr et al., 1952; Weeks et al., 1968). However, this was done under conditions where there was no freezing. In the literature reviewed, there was one field study which determined the importance of winter conditions on soil nitrate fluxes (Campbell et al., 1970), but there were no laboratory studies which dealt with the flow of soluble salts to a freezing interface.

MATERIALS AND METHODS

FIELD STUDIES

Two sites were selected for this study. They were a Red River clay located at Glenlea, Manitoba, and a Portage loam located at Westbourne, Manitoba. These soils, which were cropped the previous year, were left uncropped during the study. Some characteristics of the soils are given in Table 1. The methods employed in characterizing the soils are described by Jackson (1958).

TABLE 1. SOME PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE SOILS

	RED RIVER	PORTAGE
Texture	Clay	Loam
C.E.C. (meq/100g)	44.7	27.5
pH	6.5	8.2
Specific conductance (mmho/cm)	0.8	8.8
Cl^- (ppm)	15	410
Organic matter (%)	2.6	5.9

Field studies were carried out in 1971 over a four month period from June until October. Samples were also taken from the Red River clay in May and October, 1972. On June 1, 1971, calcium nitrate, urea and ammonium sulphate fertilizers supplying 500 lb N/acre were hand-broadcast on separate plots of the Red River clay. Fertilizer grade calcium chloride, supplying 500 lb Cl^-/acre, was also broadcast on a plot of similar size. The four plots, each 33'x 33', were adjacent to one another and occupied a total area of 1/10 acre (66'x 66'). A similar treatment was carried out on the Portage loam on June 3.

The first samples were taken one week following application of the fertilizer. Samples were taken from each of the four plots at 3 inch intervals down to the 12 inch depth and at 6 inch intervals down to the 24 inch depth. A similar sampling was carried out again one week later at both sites. Following this, sampling was carried out at two week intervals until the final sampling on October 8 on the Red River soil and October 15 on the Portage soil. The samples were taken at 3 inch intervals down to the 18 inch depth and then at 6 inch intervals down to the 48 inch depth. In 1972 samples were taken from the Red River soil in May following the spring thaw and in October prior to freeze-up. These samples were taken at 1 ft intervals down to the 8 ft depth.

Moisture determinations were made on all samples as soon as they were brought in from the field. The loss of water on drying for 24 hours at about 110C was used to calculate the percent moisture on an oven-dry soil weight basis. The remaining moist soil was stored at about 5C for one or two days until extractions were done.

Nitrate-, nitrite- and ammonium-nitrogen were extracted from the samples by shaking approximately 5 g of soil with 100 ml 2N KCl for 1 hour. The suspension was filtered using Whatman No. 42 filter paper and the filtrate used to determine NH_4^+-, NO_2^-- and NO_3^--nitrogen in the soil.

In order to extract chloride from the soil, approximately 10 g of soil were shaken with 100 ml distilled water for 30 minutes. The suspension was filtered through Whatman No. 42 filter paper and the filtrate used to determine chloride concentration in the soil.

Nitrate and nitrite were determined according to an automated procedure described by Kamphake et al. (1967), while the determination

of ammonium was done according to the method described by Jackson (1958).

Chloride was determined by an automatic potentiometric titration. The electrode combination — silver electrode/mercurous sulphate electrode — was used with standard $AgNO_3$ solution as the titrant.

LABORATORY EXPERIMENTS

Soil samples were taken from the 0 – 15 cm depth of the Red River clay and the Portage loam. These samples were air dried and crushed to pass through a 2 mm sieve and stored at room temperature.

A plexiglass cylinder 20 cm long was made by taping together twenty sections each with a length of 1 cm and an internal diameter of 3.5 cm. The bottom of the column was sealed with a brass plate.

There were two moisture treatments based on the water added to the air–dry soil. Fertilizer grade $Ca(NO_3)_2$ (0.387 g) was dissolved in 90 ml distilled water. This solution was then mixed uniformly with 300 g of the air–dry soil to give approximately 200 ppm N and bring the mixture to approximately 30% moisture in the Portage soil and 40% in the Red River soil.

One portion of the mixture was used to determine the gravimetric water content while nitrate and nitrite nitrogen were determined in another portion by the method described for the field experiment. Approximately 345 g of the remaining soil mixture were packed into the column to give a wet soil bulk density of about 1.272 g/ml. The column was placed vertically in an insulating jacket with the cold side up. The brass plate at the warm end was maintained at room temperature which was about 20C. The column was sealed at the top by a heat exchanger maintained at a constant temperature of –10C by a Haake

Model FK constant temperature circulator. Two trials lasting 7 days and 14 days respectively, were conducted on each soil.

At the end of the thermal period, the column was removed from the insulating jacket and cut into 1 cm sections. The soil in each section was mixed thoroughly and moisture, nitrate and nitrite determinations were done according to the methods described previously.

For the higher moisture treatments, 0.387 g of fertilizer grade $Ca(NO_3)_2$ was dissolved in 120 ml of distilled water and mixed uniformly with 300 g of the air-dry soil to bring the mixture to approximately 40% moisture in the Portage soil and 50% in the Red River soil. The experiment was then continued in the same way as was described for the lower moisture treatments.

At both moisture contents, a check was included for comparison with the treated soil columns. This experiment was different from those previously described only in the absence of a nitrogen source. Distilled water was added to the soil to bring it to the required moisture content and the trials were conducted at each moisture content for 7 days and 14 days.

Column studies were also carried out using $AgNO_3$ instead of $Ca(NO_3)_2$ in order to minimize the production or denitrification of inorganic nitrogen compounds in the soil. In this experiment 0.728 g of reagent grade $AgNO_3$ was dissolved in 90 ml distilled water for the lower moisture treatments and in 120 ml for the higher moisture treatments. Only two-week freezing trials were conducted.

RESULTS AND DISCUSSION

FIELD EXPERIMENT

The ionic distributions in the Red River clay and Portage loam one week after application of the fertilizers are shown in Fig. 1 and 2, respectively. During this one week interval there was 0.67 inch of rainfall at the Glenlea site and 1.75 inches at the Westbourne site.

The chloride concentration in the unfertilized Red River soil increased with depth, while the nitrate concentration was nearly constant down to the 24 inch depth of the soil profile (Fig. 1A). Due to soil and sampling variation it was not possible to determine the exact depth to which the fertilizer had penetrated. An arbitrary level of two to three times the concentration in the unfertilized soil was therefore chosen as the criterion for distinguishing soil samples containing fertilizer nitrogen from those not affected by fertilizer. On the basis of this criterion, the depths of penetration of nitrate from $Ca(NO_3)_2$ and chloride from $CaCl_2$ were nearly equal (Fig. 1B). Negligible concentrations of nitrate were found in the soils treated with urea and $(NH_4)_2SO_4$ (Fig. 1C and D). Almost all of the applied nitrogen was still in the ammonium form and retained in the surface 9 to 12 inches of the soil profile. The distributions of nitrate (Fig. 1B) and ammonium (Fig. 1C and D) in the soil profile were similar to those predicted theoretically by Cho (1971).

The chloride concentration in the unfertilized Portage soil was very high. However, nitrate concentration was similar to that of the Red River clay and was relatively low and constant throughout the soil
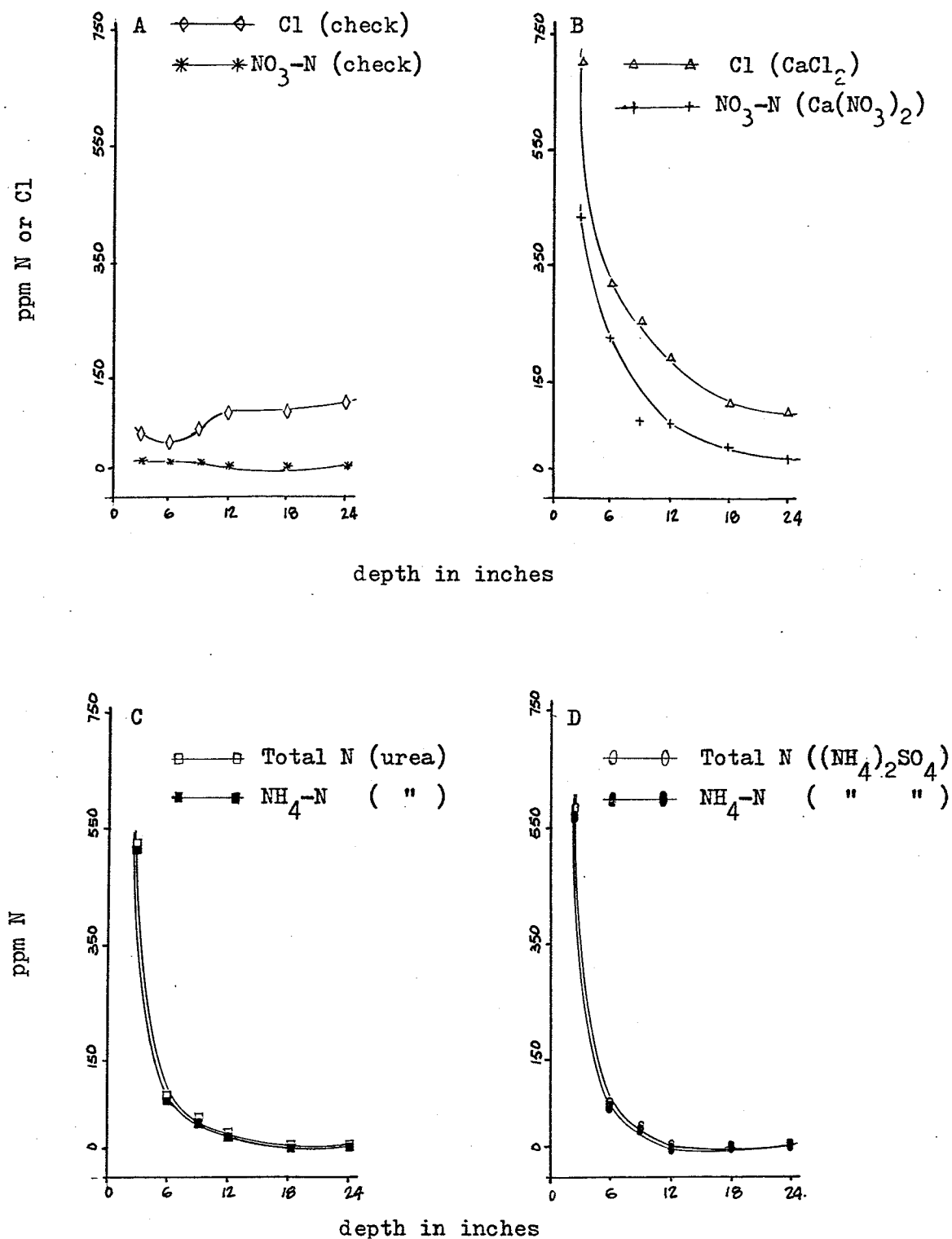
Fig. 1. Nitrogen and chloride distribution in the Red River
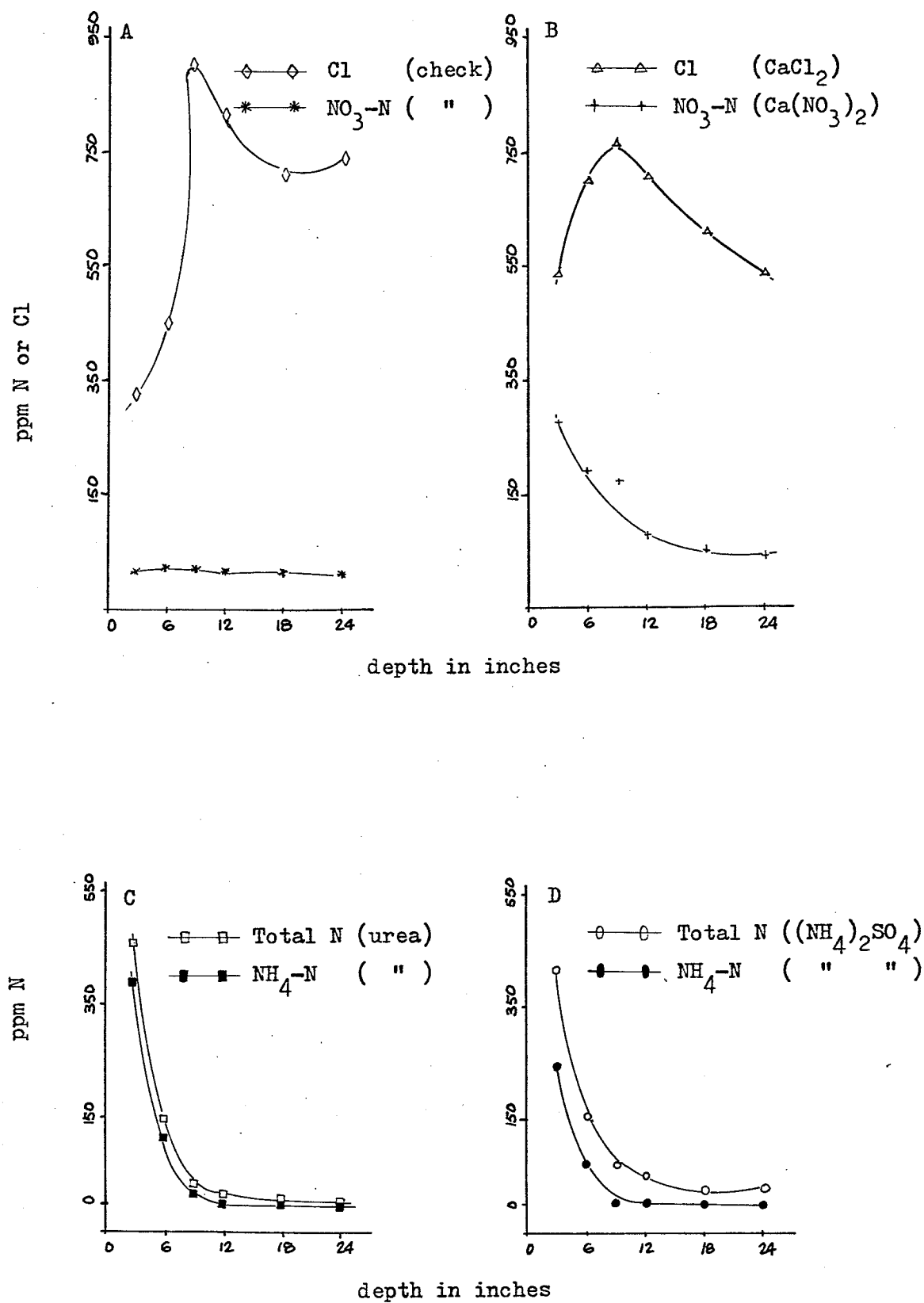clay on June 8, 1971.

Fig. 2. Nitrogen and chloride distribution in the Portage loam on June 10, 1971.

profile (Fig. 2A). The occurrence of a maximum in Cl^- concentration at the 9 inch depth of the $CaCl_2$ treated soil (Fig. 2B) did not necessarily indicate that the applied chloride had moved to that depth since this maximum also occurred in the untreated soil (Fig. 2A). Nitrate from $Ca(NO_3)_2$ penetrated to the 24 inch depth (Fig. 2B). Its distribution curve was similar to that obtained for the Red River soil.

Greater amounts of nitrate were found in the urea and $(NH_4)_2SO_4$ treated Portage soil than in the Red River soil, indicating a higher degree of nitrification in the Portage soil (Fig. 2C and D). Movement of ammonium nitrogen was limited, but because of oxidation of NH_4^+ to NO_3^- and higher rainfall, the depth of penetration of total nitrogen into the soil profile was greater for the Portage than for the Red River soil.

Results obtained throughout the duration of the field experiment were analysed for depth of nitrogen penetration and magnitude of nitrogen recovery. Depths of nitrogen penetration into the Red River soil profile from the different fertilizer sources and rainfall data are shown in Table 2. The data showing the distribution of nitrogen as a function of depth are shown in the Appendix.

Chloride penetrated to the 20 inch depth during the first seven days after application and to the 24 inch depth 2 weeks after application. During this time interval, the behaviour of chloride and nitrate appeared to be identical. However, chloride transport into the soil profile could not be determined after these dates due to the high concentration of Cl^- in the lower depths of the unfertilized soil.

During the summer period (June to September), nitrate in the

TABLE 2. APPROXIMATE DEPTHS OF FERTILIZER NITROGEN PENETRATION IN THE RED RIVER CLAY ON VARIOUS SAMPLING DATES

Sampling date	Depth of Penetration (ins)				Rainfall (ins)
	$CaCl_2$	$Ca(NO_3)_2$	Urea	$(NH_4)_2SO_4$	
June 8, 1971	20	20	12	10	0.67
June 15, 1971	24	24	18	15	0.48
June 29, 1971	-	24	12	12	0.76
July 13, 1971	-	18	18	15	1.39
July 27, 1971	-	18	15	15	1.86
August 11, 1971	-	18	18	18	0.20
August 25, 1971	-	20	24	12	1.32
September 8, 1971	-	15	18	18	1.08
October 8, 1971	-	30	30	24	2.26
May 3, 1972	-	24	24	18	-
October 17, 1972	-	40	40	-	-

$Ca(NO_3)_2$-treated plot appeared to remain stationary or move upward in the soil profile. High rainfall in October and most likely a lower evaporation rate resulted in downward movement of nitrate to the 30 inch depth. Sampling was not conducted during the winter period.

Nitrate distribution in the soil in May 1972 suggested that during the winter period either nitrate moved upward or was lost through denitrification. The transfer of moisture and dissolved nitrate to the surface could also have been accomplished through freezing in the winter. Results obtained in October 1972 indicated that nitrate moved down to the 40 inch depth. Thus the net effect of rainfall between May and October was the same as in 1971. Nitrate penetrated to lower depths in the fall than in the spring.

The depths of penetration of nitrogen into the urea and $(NH_4)_2SO_4$ treated soil were reported for total nitrogen rather than for ammonium and nitrate nitrogen separately, since such a separation would have been difficult. On both plots the degree of nitrogen penetration was considerably less than that of nitrogen from $Ca(NO_3)_2$ during the first four weeks after application. This was due to the occurrence of nitrogen predominantly in the ammonium form. However, the differences in degree of penetration among the fertilizers decreased by mid-July. There was some variation in the depth of nitrogen penetration on different sampling dates, but there was no apparent relationship to rainfall. On both the urea and $(NH_4)_2SO_4$ plots, extensive penetration in the fall similar to that observed on the $Ca(NO_3)_2$ plot could have been due to high rainfall and reduced evaporation from the soil surface during this period.

Nitrogen distribution patterns in the fertilized plots remained

essentially unchanged during the summer period (Fig. A1 to A14).
Nitrogen was concentrated at the surface during this time and its
distribution was generally not affected by the small changes occurring
at lower depths. Fluctuating surface levels were attributed to field
variation. Rainfall in October transferred the maximum in the nitrogen
curve to the 9 to 12 inch depth of all plots except the ammonium
sulphate-treated Red River plot (Fig. A15 and A16). On this plot
the NO_3^- maximum (the difference between total and NH_4^+-N) was trans-
ferred from the surface, but because of the high NH_4^+ concentration
at the surface, the total nitrogen distribution curve did not change.
Nitrate was the only form of nitrogen recovered in the Red River soil
in May 1972 and was still concentrated in the surface 12 inches of
the soil profile (Fig. A17). In October 1972 downward movement of
the nitrate maximum was only observed in the $Ca(NO_3)_2$ treated soil
(Fig. A18).

The degree of penetration of nitrate from surface-applied
$Ca(NO_3)_2$ into the Portage loam (Table 3) was generally greater than
that in the Red River soil. Within a month after the application,
nitrate from $Ca(NO_3)_2$ had penetrated to the 30 inch depth, and to
the 42 inch depth two months after application. Total rainfall
during this period was 6.37 inches. During August, a period of low
rainfall, an upward movement of nitrate was detected. This was also
observed for the Red River soil.

The behaviour of Cl^- was not compared to that of NO_3^- in the
Portage soil. The very high concentrations of Cl^- found in this
soil precluded an attempt to trace water movement using the Cl^- ion.

TABLE 3. APPROXIMATE DEPTHS OF FERTILIZER NITROGEN PENETRATION IN THE PORTAGE LOAM ON VARIOUS SAMPLING DATES

Sampling date	Depth of Penetration (ins)			Rainfall (ins)
	$Ca(NO_3)_2$	Urea	$(NH_4)_2SO_4$	
June 10, 1971	24	12	14	1.75
June 17, 1971	24	18	24	1.04
July 1, 1971	30	18	18	0.80
July 15, 1971	36	18	36	1.53
July 30, 1971	42	18	24	1.25
August 13, 1971	42	18	36	0
August 27, 1971	30	12	24	0.62
September 10, 1971	30	24	36	1.03
October 15, 1971	36	30	42	1.85

Penetration of nitrogen from urea was about one-half as great

as penetration from $Ca(NO_3)_2$ throughout the summer period. However,

with the approach and arrival of the fall season the depth of penetra-

tion increased until it was nearly equal to that of $Ca(NO_3)_2$.

Nitrogen penetration from $(NH_4)SO_4$ was intermediate between

penetration from $Ca(NO_3)_2$ and that from urea in the early periods of

the experiment. As time elapsed, however, the behaviour of $(NH_4)_2SO_4$

seemed similar to that of $Ca(NO_3)_2$.

The amounts of NH_4^+-N and NO_3^--N in the Red River soil profile

down to the depth of penetration were calculated and tabulated (Table 4).

The total quantity of nitrogen recovered at various times was very

variable. In many instances the amount of nitrogen recovered in the

soil exceeded the amount of nitrogen applied. Possible reasons for

this are the inhomogeneity of fertilizer application and cracks in

the soil surface.

Nitrogen recovery in the $Ca(NO_3)_2$ treated soil up to the end

of July 1971 was assumed to be around 100 percent even though the

actual figures represented a recovery of more than 100 percent. The

concentration of nitrogen in the soil decreased from July 1971 to

October 1972. Recovery after the winter period was only approximately

200 lb/acre (40%). Since there was no evidence that nitrate had

penetrated beyond the depths sampled it is reasonable to assume that

denitrification and possibly immobilization were responsible for the

disappearance of nitrate.

In the discussion of the data in Table 2, it was suggested

that the apparent movement of nitrate upward in the soil treated with

TABLE 4. QUANTITIES OF NO_3^- AND NH_4^+ NITROGEN IN FERTILIZED
RED RIVER CLAY ON DIFFERENT SAMPLING DATES

Sampling dates	Ca(NO$_3$)$_2$	Urea		(NH$_4$)$_2$SO$_4$	
	NO_3^--N	NH_4^+-N	NO_3^--N	NH_4^+-N	NO_3^--N
	lb N per acre				
June 8, 1971	900	600	0	380	0
June 15, 1971	1060	240	80	220	180
June 29, 1971	1560	490	340	1240	100
July 13, 1971	920	540	600	1200	100
July 27, 1971	640	410	670	30	100
August 11, 1971	330	60	270	380	290
August 25, 1971	300	120	500	90	280
September 8, 1971	460	140	440	660	160
October 8, 1971	490	0	240	300	250
May 3, 1972	240	0	40	0	20
October 17, 1972	180	0	280	0	20

$Ca(NO_3)_2$ may have been due to the effects of rainfall and evaporation. However, the decrease in nitrate levels in July and August (Table 4) occurring at the same time suggests that both climatic conditions and the depletion of nitrate through immobilization and denitrification could have been factors contributing to loss of nitrogen from lower depths.

Total nitrogen concentrations in the urea and $(NH_4)_2SO_4$ plots were generally not as high as in the $Ca(NO_3)_2$ plot. This may have been due in part to volatilization of N as NH_3 from the urea and $(NH_4)_2SO_4$ treated soils. Ammonium levels did not decrease appreciably with urea until the end of July. Ammonium concentrations from $(NH_4)_2SO_4$ were variable and persisted for the entire 1971 sampling period. Nitrate concentrations above the check levels were not detected in the urea and $(NH_4)_2SO_4$ treated plots on June 8. However increased nitrate concentrations were detected subsequently, and the concentrations increased on each sampling date until August 1971. The rate of nitrate production in the Red River soil was more rapid from urea than from $(NH_4)_2SO_4$. Ammonium nitrogen was not detected in the urea plot after the September 8 sampling, while it remained in the $(NH_4)_2SO_4$ plot until October 8 - the final sampling date of 1971.

The effect of rainfall on nitrogen penetration in 1971 could not easily be observed for most of the experiment because the applied urea and $(NH_4)_2SO_4$ were still in NH_4^+ and NO_3^- forms. Until mid-July, total nitrogen penetration into the soil was less than in the $Ca(NO_3)_2$ plot because of NH_4^+ retention near the surface. However, as nitrate concentration increased from around mid-July, the depth of nitrogen penetration increased and became almost equal to that observed in

the $Ca(NO_3)_2$ plot. Rainfall between September 8 and October 8 resulted in a smaller increase in N penetration in the $(NH_4)_2SO_4$ plot than in the urea plot. This was probably due to the relatively small percentage of total nitrogen in the mobile NO_3^- form.

Nitrate levels on the fertilized Red River plots in the spring of the year following application were low, probably as a result of denitrification or immobilization. None of the ammonium nitrogen remaining in the soil in the fall of 1971 was recovered in 1972. This too might have been immobilized in the soil organic matter. Higher nitrate concentrations obtained in the fall sampling of the urea plot were probably due to variation in the field.

Nitrogen levels in the Portage soil, like in the Red River soil, generally exceeded the rate at which it was applied (Table 5). Unlike the Red River soil, however, nitrate concentration remained high throughout the 1971 experimental period and there was no evidence of denitrification or immobilization. Therefore in comparison to the Red River clay (Table 2), the results shown in Table 3 should allow a better estimate of the relative importance of the effects of soil characteristics and climate on the depth of nitrate penetration into the Portage soil.

Total nitrogen levels on the urea and $(NH_4)_2SO_4$ plots were not as high as on the $Ca(NO_3)_2$ plot. Nitrate concentration was higher and the ratio of NO_3^- to NH_4^+ greater from $(NH_4)_2SO_4$ than from urea. Thus the greater depth of N penetration from $(NH_4)_2SO_4$ than from urea (Table 3) could be attributed to its more rapid oxidation rate. Ammonium nitrogen was not detected in either the urea or $(NH_4)_2SO_4$ plot after July 30.

TABLE 5. QUANTITIES OF NH_4^+ AND NO_3^- NITROGEN IN FERTILIZED
PORTAGE LOAM ON DIFFERENT SAMPLING DATES

Sampling dates	$Ca(NO_3)_2$	Urea		$(NH_4)_2SO_4$	
	lb N per acre				
	NO_3^-	NH_4^+	NO_3^-	NH_4^+	NO_3^-
June 10, 1971	660	420	140	250	290
June 17, 1971	1120	360	230	20	640
July 1, 1971	1310	240	640	450	1470
July 15, 1971	980	130	70	80	1080
July 30, 1971	1640	60	310	20	490
August 13, 1971	1640	0	580	0	1500
August 27, 1971	1260	0	80	0	1440
September 10, 1971	580	0	360	0	580
October 15, 1971	920	0	700	0	960

This earlier disappearance of NH_4^+ and the generally higher NO_3^- to NH_4^+ ratios than in the Red River soil suggested a more rapid nitrification rate in the Portage soil.

The results of the field experiment indicated that there were differences in nitrogen movement which could be attributed to soil and fertilizer. The depth of nitrogen penetration was greatest from $Ca(NO_3)_2$ in both soils. Penetration of nitrogen was greater in the Portage loam than in the Red River clay. The differences between the two soils was most marked during the periods when rainfall was limiting or evaporation was likely to be high. There were no wet periods at either site until early October. Nitrogen concentration at the surface remained high until rainfall in October caused a transfer of the maximum nitrogen concentration to lower depths (Fig. A15 and A16). Decreases in depths of nitrogen penetration during the summer in the Red River soil, and during a period of low rainfall in the Portage soil (August and September) were taken as indicators of upward movement of nitrogen.

Recovery of NO_3^- from urea and $(NH_4)_2SO_4$ varied through the season. Depth of N penetration was determined to some extent by the rate of oxidation of NH_4^+ to the more mobile NO_3^- form. A more rapid nitrification rate and higher nitrate levels in the Portage soil resulted in a greater degree of penetration of nitrogen than in the Red River soil. Nitrate concentrations in the Portage soil were higher, and the rate of nitrification more rapid with $(NH_4)_2SO_4$ than with urea. The reverse was true for the Red River clay. Migration of ammonium nitrogen from the point of application was restricted in both soils. The decrease in nitrate levels by the fall of 1971 through immobilization or

denitrification was more marked in the Red River clay.

In both soils the quantity of fertilizer added was high in relation to native soil nitrogen, but this was not true for chloride. Thus a comparison of movement of surface-applied Cl^- and NO_3^- could not be made.

Generally the study of the downward movement of surface-applied nitrogen showed that nitrogen on the surface of the soil was not easily moved downward during the summer period. However, some increases in concentration at lower depths along with a decrease in the total quantity in the soil indicated that surface-applied N moved downward with probable denitrification and immobilization.

LABORATORY EXPERIMENTS

The moisture distribution patterns in the Red River soil columns subjected to the thermal gradient at 44 percent initial moisture content are shown in Fig. 3.

The depths of freezing after one week were 4 cm and 5 cm in the untreated and $Ca(NO_3)_2$-treated soil columns, respectively (Fig. 3A and C). A net movement of moisture into the frozen soil of both columns was indicated by an increase in moisture content over the initial moisture level. The point of maximum moisture content was also the point of occurrence of a very dense ice phase from which much of the soil was excluded. The magnitude of ice accumulation after one week was nearly equal in the two columns. The sharp increase in moisture content at the freezing front suggested that ice accumulation took place in a stationary zone. The moisture content in the frozen zone was generally higher than the initial value but far less than that

at the ice front. This implies that moisture movement toward the freezing front was slow compared to the rate at which the freezing front progressed from the cold end of the column to the stationary front.

The moisture distribution in the unfrozen soil was more or less uniform in both the treated and untreated Red River soil columns.

There was no significant change in the moisture distribution with an increase in the duration of the cold treatment (Fig. 3B and D). Lower moisture contents at the ice front of the two week treatments compared to the one week treatments might have been due to experimental errors. Such errors could have been introduced through non-uniform packing, inefficient insulation or fluctuations in the cold plate temperature as well as room temperature.

The moisture distribution curves in the Red River soil columns initially at 54 percent moisture content (Fig. 4) show some of the characteristics of the curves obtained at the lower moisture content (Fig. 3). Maximum moisture contents occurred at the freezing front and relatively low moisture contents beyond it. However, the moisture content increased from just beyond the frozen front toward the warm end of the column. Such a moisture gradient was not evident at the lower initial moisture content. The magnitude of the moisture gradient in the unfrozen soil decreased with an increase in the duration of the experiment, indicating that more moisture was transported to the frozen front. Net moisture transfer from warmer to colder portions of the column was less than at the lower initial moisture content.

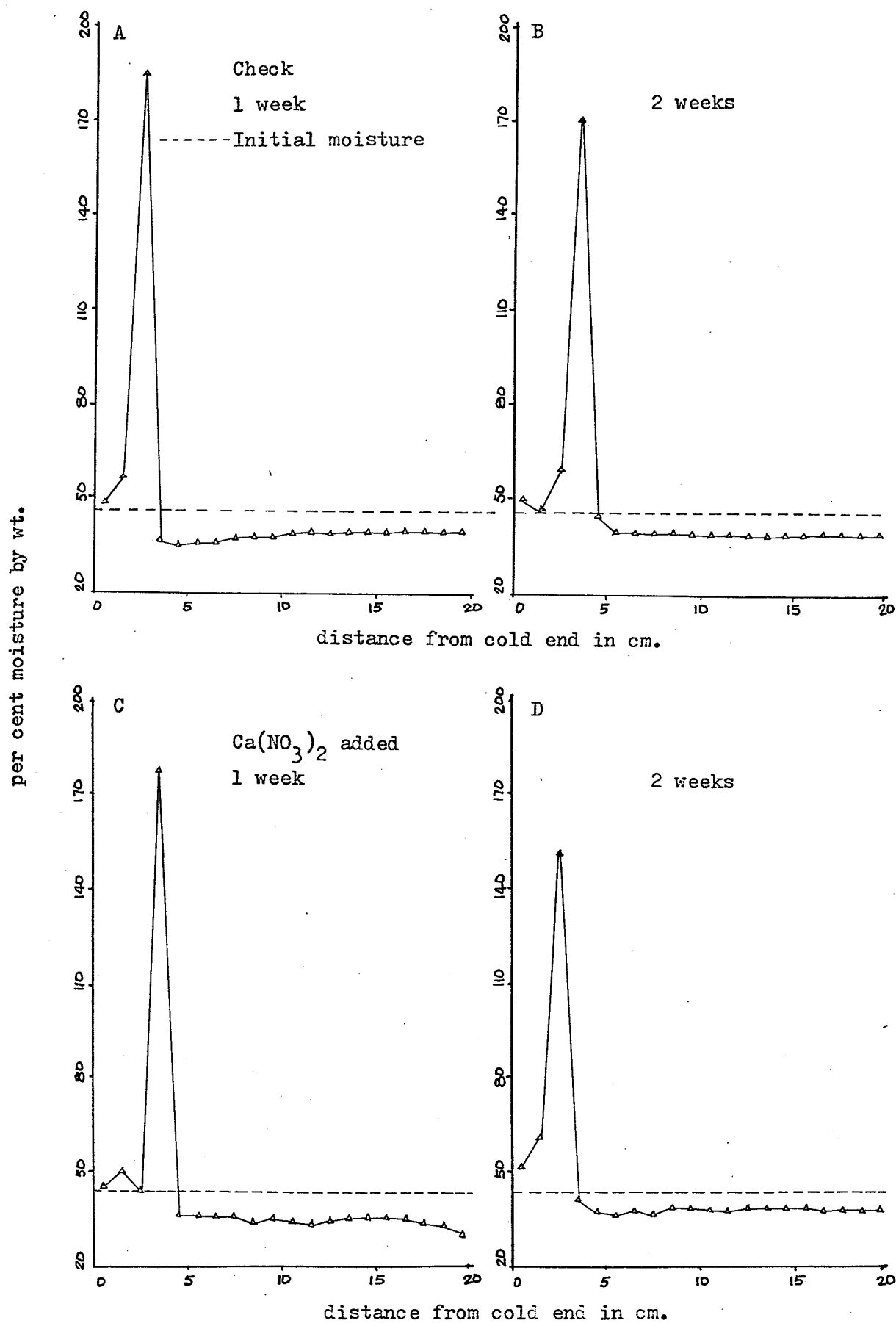The moisture distribution in $AgNO_3$ - treated Red River soil columns

Fig. 3. Moisture distribution in Red River soil columns after being subjected to the thermal gradient (initial moisture content = 44%).
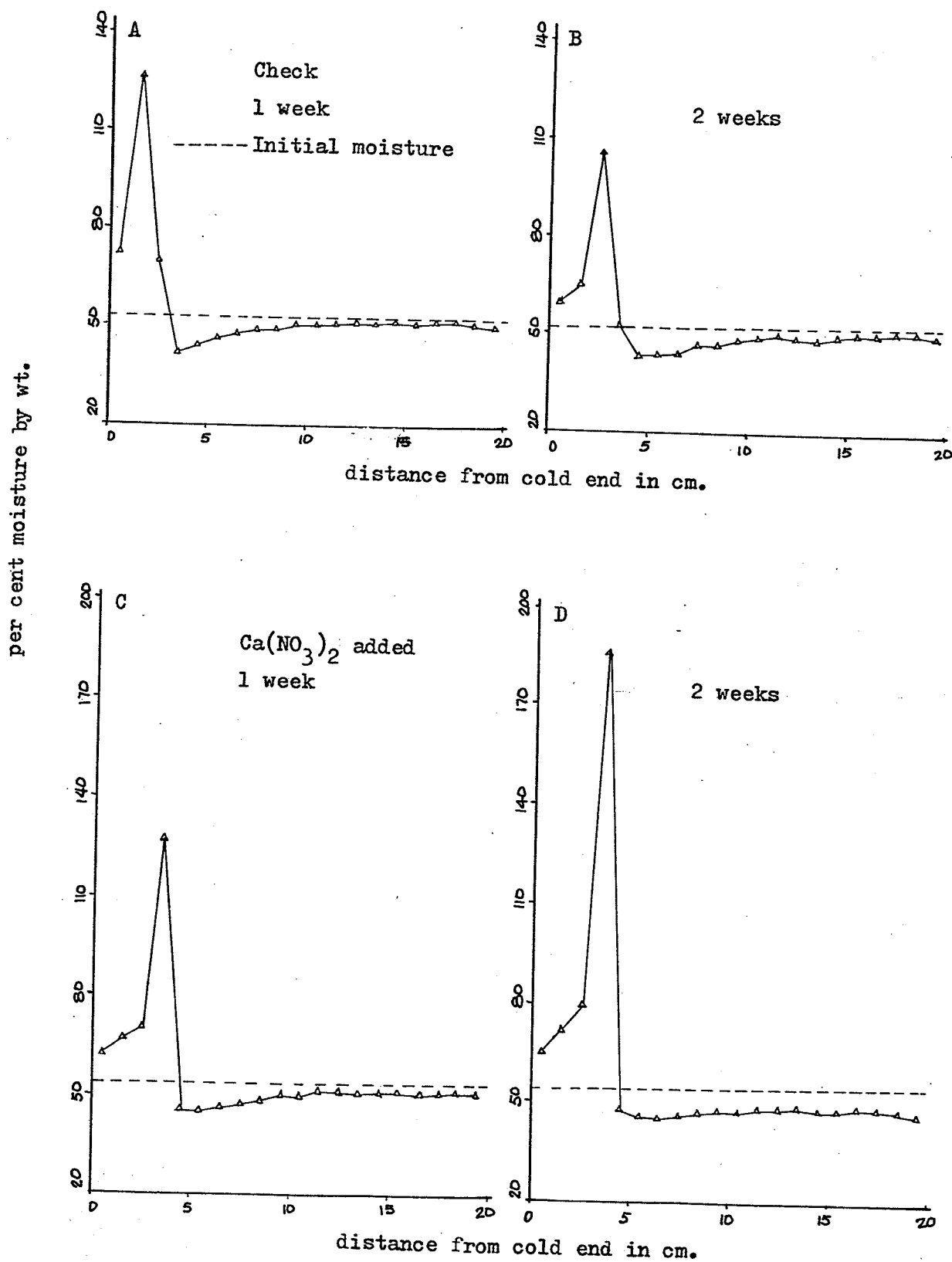
60

Fig. 4. Moisture distribution in Red River soil columns after being subjected to the thermal gradient (initial moisture content = 54%).
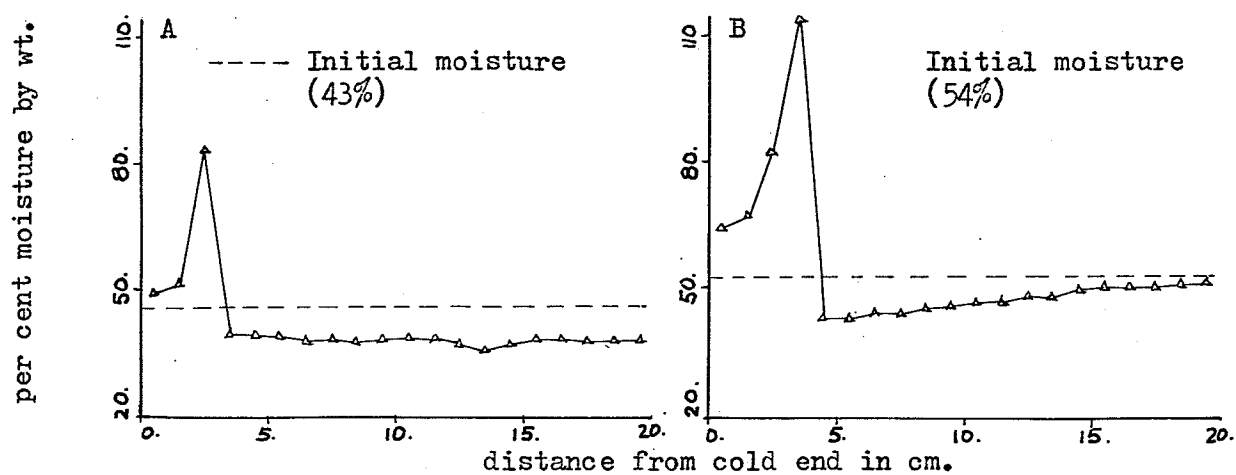
Fig. 5. Moisture distribution in AgNO$_3$-treated Red River soil columns after being subjected to the thermal gradient.

initially at 44 percent and 54 percent moisture are shown in Fig. 5.
Both columns were exposed to the temperature gradient for a period
of two weeks. There was a sharp discontinuity at the freezing front
of the moisture content profile similar to that observed in untreated
and $Ca(NO_3)_2$-treated soil columns. The occurrence of a moisture grad-
ient in the unfrozen portion of the wetter soil column (Fig. 5B), as
well as the relatively greater decrease in the moisture content of
the unfrozen portion of the drier column (Fig. 5A) was also observed
previously (Fig. 3 and 4).

The distribution of moisture in the Portage soil columns sub-
jected to the temperature gradient at 33 percent initial moisture
content is shown in Fig. 6. The data indicated a net transfer of
moisture from the warmer to the colder soil. The depth of penetra-
tion of the ice front was 4 to 5 cm in all the columns. The maximum
moisture content at the ice front was less than in the Red River soil,
and there were no visible ice lenses formed. The moisture content
in the unfrozen zone of the one week treatments (Fig. 6A and C) was
relatively constant, as was observed in the Red River soil at 44
percent moisture (Fig. 3). About one-half of the moisture initially
in the unfrozen portion of the column was transported to the frozen
zone.

The moisture distribution in the Portage soil changed with an
increase in the length of the freezing period. Very low moisture
levels in the bottom 10 cm of the column and an increase in moisture
content in the surface 10 cm provided evidence of continued transport
of moisture from warmer to colder sections of the column. A steady-

state moisture distribution was evidently not attained within the two week period.

The results of the 43 percent moisture treatments using untreated and $Ca(NO_3)_2$-treated Portage soil columns are shown in Fig. 7. High moisture levels in the frozen soil were due to moisture movement into the frozen zone. A sharp peak in the moisture distribution curve was obtained in the untreated soil column after one week of exposure to the temperature gradient (Fig. 7A). This suggested an accumulation of moisture in a stationary zone. However, the absence of such a sharp peak in the $Ca(NO_3)_2$-treated soil column (Fig. 7C) was similar to that of the column at a lower moisture content (Fig. 6C).

The moisture content at the ice front was considerably less than that obtained in the Red River soil at a similar initial moisture content. The moisture content beyond the ice front was relatively constant (Fig. 7A and C). There were no noticeable moisture gradients.

The moisture content of the frozen portion of the untreated column after two weeks of exposure to the temperature gradient (Fig. 7B) was higher, and that of the unfrozen soil lower than after one week of the cold treatment. Thus moisture transport to the frozen soil of the untreated Portage soil column was greater during the longer freezing period. However, in the $Ca(NO_3)_2$-treated soil (Fig. 7D), there was no evidence of this prolonged transport. The moisture content of the unfrozen soil of both columns was nearly constant.

The moisture distributions in Portage soil columns treated with $AgNO_3$ and subjected to the temperature gradient for two weeks are shown in Fig. 8. The moisture content of the unfrozen portion of
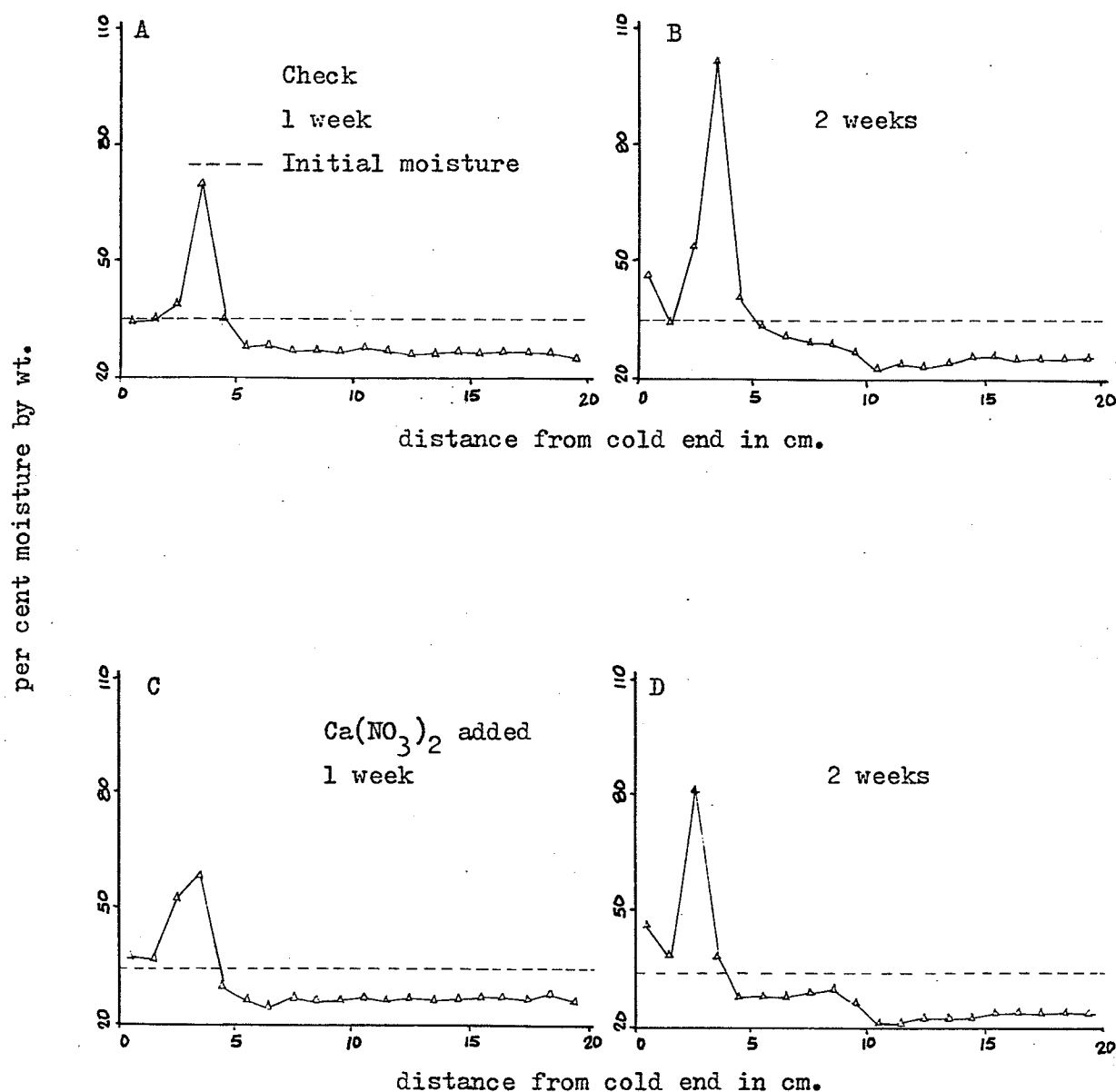
Fig. 6. Moisture distribution in Portage soil columns after being subjected to the thermal gradient (initial moisture content = 33%).
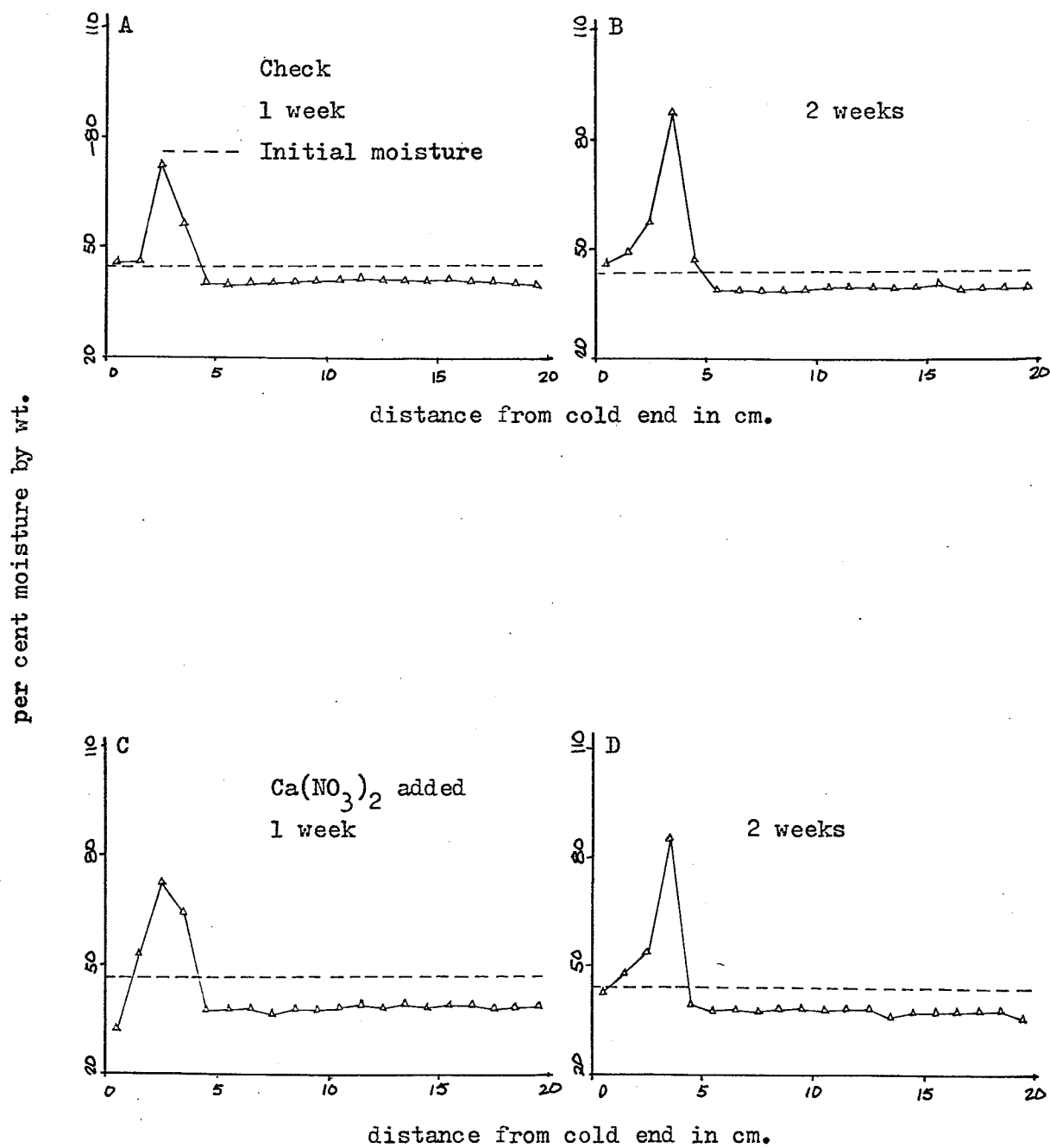
Fig. 7. Moisture distribution in Portage soil columns after being subjected to the thermal gradient (initial moisture content = 44%).
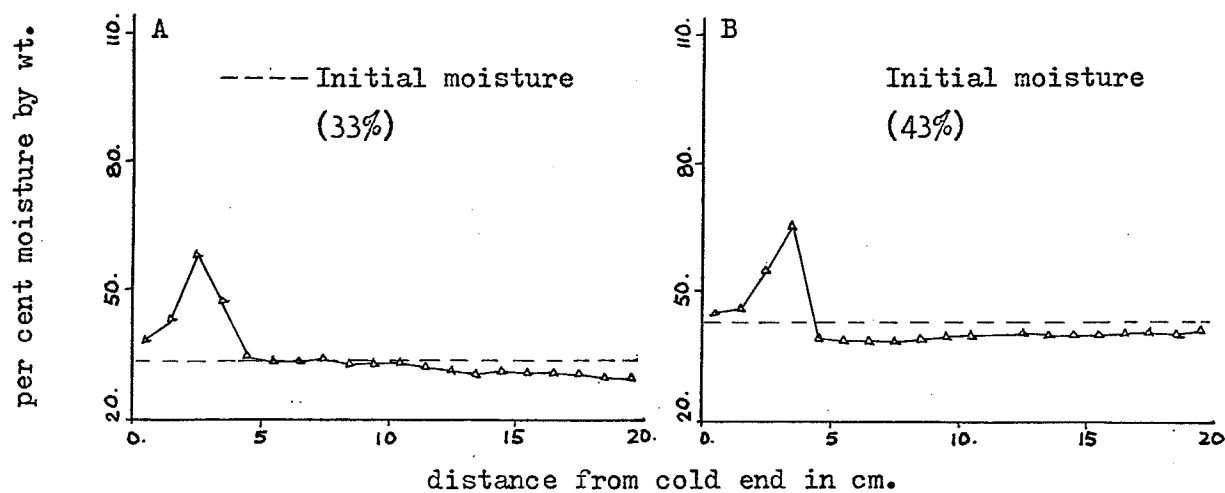
Fig. 8. Moisture distribution in AgNO₃-treated Portage soil columns after being subjected to the thermal gradient.

the column initially at 33 percent moisture (Fig. 8A) showed a gradual decrease with increasing depth away from the ice front. This was similar to what was observed in the untreated and $Ca(NO_3)_2$-treated Portage soil columns subjected to the temperature gradient for the same two week period at the same moisture content (Fig. 6B and D). The moisture distribution at the higher moisture content (Fig. 8B) was similar to that obtained in $Ca(NO_3)_2$-treated and untreated Portage soil columns at 43 percent moisture content (Fig. 7B and D).

Moisture movement from the warmer to the colder end of the column was evident in all the experiments. There was generally an increase in the moisture content of the frozen zone far above and a decrease in the unfrozen zone far below initial moisture levels. There was a moisture gradient in the unfrozen zone of some Red River soil columns (Fig. 4, 5B) with the lowest moisture content occurring at the boundary between frozen and unfrozen soil. The frozen soil extracted moisture from the unfrozen soil beginning with the first appearance of ice. When movement into the frozen soil was very rapid and the flow of water into the region suffering the moisture loss was slow, a depression in the moisture profile formed below the freezing front. This situation was evident in Fig. 4 and Fig. 5B.

There was no evidence of a relationship between depth of freezing and initial moisture conditions, or between depth of freezing and duration of the experiments. Differences in depths of freezing were observed in columns which were initially at the same moisture content and nitrate levels, and subjected to the temperature gradient for the same length of time. It is likely that observed differences

were the result of variable experimental conditions.

There was also no real difference in depth of freezing between the Red River and Portage soil columns. The most striking difference between the soils was in the degree of ice accumulation, which was much greater in the Red River soil even when both soils were at comparable initial moisture conditions. All Red River soil columns showed a very sharp discontinuity in the vicinity of the ice front. This was not quite as marked in the Portage soil. There was also a difference in the type of frost formed in the two soils. The ice lenses which formed just behind the freezing interface in all the Red River soil columns consisted of a very dense ice phase from which much of the soil was excluded. Such ice lenses would have acted as a barrier to any further movement past them once they were formed. In the Portage soil the frost was of a more porous nature. The formation of large ice lenses at the stationary front was probably dependent upon the soil characteristics rather than the initial moisture content. It could have been that the smaller average pore size in the fine-textured Red River clay favoured the formation of ice lenses. The results indicated that, in some instances, (Fig. 6C and Fig. 7C), the frozen Portage soil was still permeable to water so that the moisture content in the frozen zone increased with time. It is known that a significant amount of flow can occur in the frozen soil (Hoekstra, 1969; Mosiyenko, 1958; Stepanov, 1957; Tyskin, 1956).

The effect of moisture content on moisture transport was different for the two soils. Net moisture movement toward the surface was expected to be more pronounced in the wetter soil since this

effect was demonstrated by Pelton et al., (1967) and Campbell et al., (1970) in their research at Swift Current Saskatchewan. However, this trend was not evident in either Red River or Portage soil columns. It may have been that the moisture contents employed in the experiments were high enough to make this moisture effect negligible or totally absent. In the Red River soil, net moisture movement and especially the degree of ice accumulation were less at the higher moisture content. In this case there was the possibility of reduced net permeability of moisture in the more saturated soil.

The effect of the length of the freezing period on moisture distribution in the Red River soil was evident in the wetter soil columns. At this moisture content (54%), the moisture gradient observed in the unfrozen portion of the columns during the first week of freezing was partially or completely dissipated with time. The effect of the length of the exposure period on moisture distribution was not apparent in the wetter Portage soil columns. However, at the lower moisture content (33%), increasing the period of exposure to the temperature gradient resulted in increased net transport to the freezing front.

Nitrate and nitrite distributions in the $Ca(NO_3)_2$-treated Red River soil initially at 44 percent moisture are shown in Fig. 9. The results obtained with the untreated soil columns are shown in the Appendix (Fig. A19). The concentrations of nitrate and nitrite were plotted on an oven dry soil basis as well as on a solution basis in order to analyse the physical process of nitrogen transport to a freezing front.

The distribution of nitrate on a dry soil basis, after one week

of the cold treatment, showed an accumulation of nitrate in the frozen zone especially near the stationary ice front. Beyond the frozen zone, there was a sharp decrease in nitrate concentration followed by a gradual increase toward the warm end of the column.

The results obtained after two weeks of the cold treatment (Fig. 9B) showed characteristics similar to those obtained in the one-week treatment. However, the magnitude of the gradient in the unfrozen zone was not as great as in the one-week treatment.

Nitrate distribution in the one-week experiment when expressed on a solution basis was different from that expressed on a dry soil basis (Fig. 9A). This was especially true in the frozen zone where the concentration of nitrate in solution was generally lower than the initial value. A minimum value occurred at the point of greatest ice accumulation. Beyond this point the concentration increased to a maximum and then decreased. This was followed by a gradual increase with depth, with a maximum value occurring in the warmest portions of the soil column. The distribution in the two-week experiment (Fig. 9B) showed a similar pattern except for the shift of the point of minimum nitrate concentration in the unfrozen zone toward the warmer end.

Only a trace of nitrite was detected in the Red River soil (Fig. 9C and D). Total nitrogen recovery was nearly 100 percent (Table 6).

Since total nitrogen remained constant in the Red River soil at 44 percent initial moisture content, depletion or accumulation of nitrate at various locations in the column must have been due to
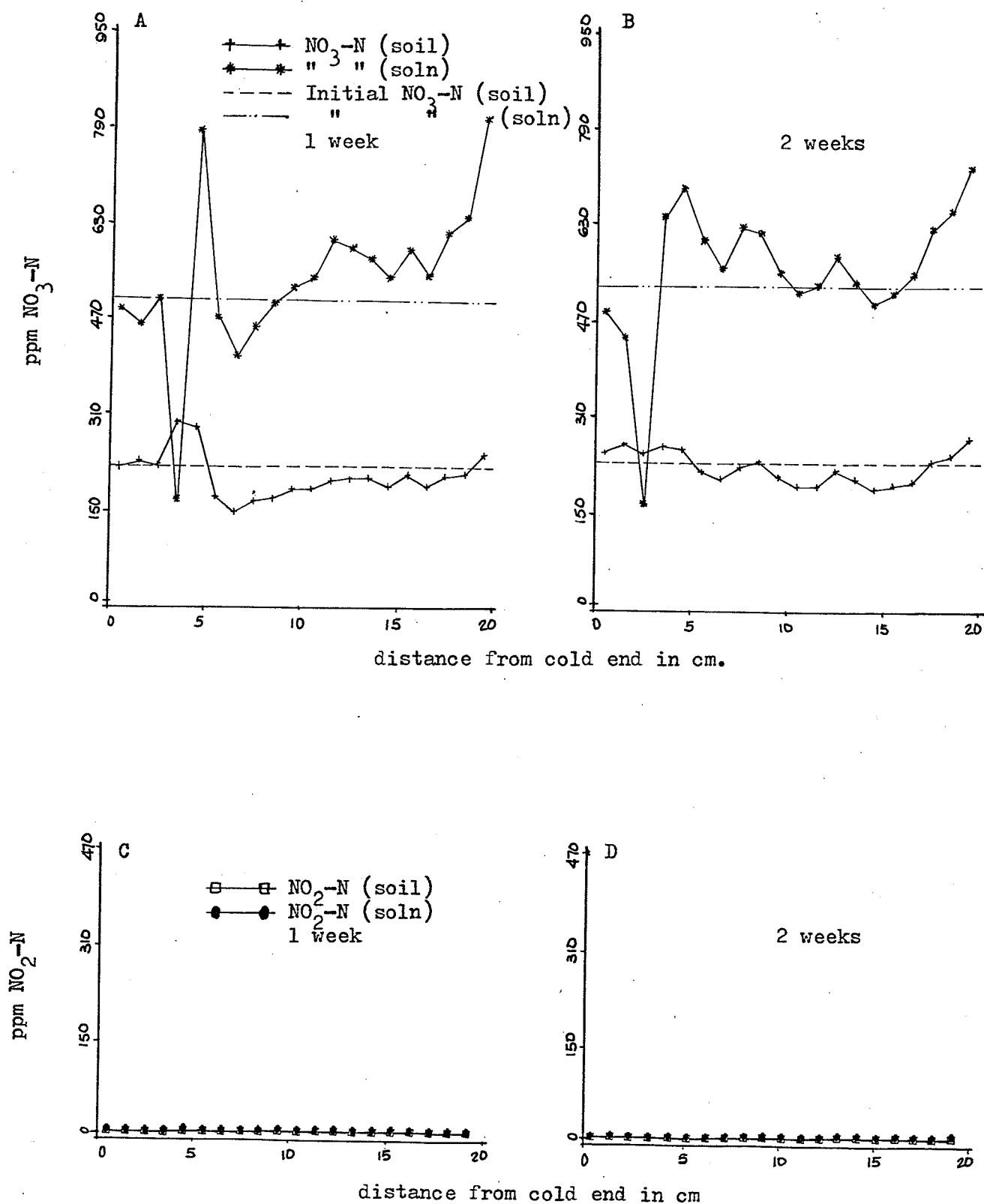
Fig. 9. Distribution of NO_3^- and NO_2^- in $Ca(NO_3)_2$-treated Red River soil columns after being subjected to the thermal gradient (initial moisture content = 44%).

transport phenomena. Nitrate redistribution under non-isothermal conditions may be caused by 1) liquid transport, 2) vapour transport, 3) exclusion of nitrate from the ice phase and 4) thermal diffusion of dissolved nitrates (Soret effect).

It has been demonstrated that under a thermal gradient, liquid will move from warmer to colder regions of a soil column (Dirksen, 1966). This liquid may contain dissolved salts which will also move from warmer to colder areas of the soil. If this were the mechanism of nitrate transport, the distribution of nitrate on a solution basis should remain constant, while the distribution of nitrate on a soil basis should follow the moisture distribution. The increase in nitrate concentration based on the dry soil weight in the frozen zone (Fig. 9A and B) indicated transport by liquid which moved to the colder zone and was immobilized as ice. However, the changes in concentration of nitrate in solution from the original concentrations (dashed lines) could not be explained by liquid transport alone.

Vapour transport from warmer to colder zones of a soil column generally results in a circulatory movement of soil moisture. There is a net evaporation in the warmest segments and a net condensation in the coldest segments of the column, with the liquid thus produced moving from colder to warmer zones of the column. If such a mechanism of moisture transport were in operation in the Red River soil, a minimum nitrate concentration on a soil basis as well as on a solution basis should be located at the point of net condensation, and nitrate con-centration should increase towards the warm end of the column. In the Red River soil (Fig. 9A and B), there was a minimum in nitrate concen-

tration in solution at the ice front or point of maximum condensation, and a gradual increase in concentration with depth in the warmer portion of the column. These characteristics suggest that vapour transport may have been partially responsible for nitrate redistribution in the soil columns.

Freezing of water can cause an exclusion of salt from the ice phase and its concentration in the residual liquid. If such an exclusion should take place during freezing of the soil, nitrate concentration in the frozen zone should show a decrease based on both soil and solution. There should also be an increase in nitrate concentration outside the ice phase. The increase in nitrate concentration beyond the ice front (Fig. 9A and B) suggests that some nitrate was excluded from the ice. However, in the frozen zone the decrease in nitrate concentration in solution could have been due to vapour transport or exclusion of nitrate from the ice or both.

Most dissolved salts will spontaneously diffuse through a solution from warmer to cooler areas (Soret effect). Soret coefficients for many salts in pure solution have been calculated by Snowdon and Turner (1961). Such an effect may occur in soils, although this has not been reported. The Soret effect cannot be studied in soils under unsaturated conditions since free convection should be absent in order to observe this effect. If there were thermal diffusion in the Red River soil, this should appear as an increase in nitrate concentration near the surface for positive Soret coefficients and an increase in the warmer soil for negative Soret coefficients.

Interpretation of the experimental results was based on the

above discussion. The results indicated that in the initial stages

of the experiment both liquid and vapour moved toward the freezing

zone. As the arriving moisture froze, some nitrate was trapped

within the soil particles. However, when the ice front became

stationary and the ice crystals started to grow, nitrate was excluded

from the ice. After a steady temperature distribution was attained

and ice ceased to form, circulatory flow became important. This

involved vapour movement to the cold end and a return flow to the

warm end in the liquid phase. Consequently nitrate accumulated in

the warmest portions of the column. Nitrate diffusion in the frozen

soil remained essentially unchanged with time.

Nitrate and nitrite distributions in the $Ca(NO_3)_2$-treated Red

River soil at the higher moisture content (54%) are shown in Fig. 10.

The results obtained in untreated columns at the same moisture content

are shown in Fig. A20.

Nitrate movement to the frozen zone was indicated in both one-

week and two-week treatments. Even though total nitrogen recovery

was less at the higher moisture content (Table 6), nitrate concentration

on a soil basis in the frozen portion of these columns was higher

than in similarly treated columns at a lower moisture content (Fig.

9A and B). Thus nitrate movement to the frozen soil increased with

an increase in the moisture content of the soil.

Nitrate concentration in the frozen soil was almost equal in

the two columns (Fig. 10A and B). This suggests that there was no

movement past the ice lens once it was formed during the first week.

The position of maximum concentration of nitrate based on the dry soil

weight occurred at the point of greatest ice accumulation. However, nitrate concentration in solution was lowest at this point. This dilution, either through vapour condensation or exclusion from the ice phase, was also observed in the drier soil columns (Fig. 9A and B).

Nitrate concentration in solution was high immediately outside the frozen zone of both columns. In the one-week treatment (Fig. 10A) this could have been due partly to liquid transport of nitrate to those depths or partly to exclusion of nitrate from the ice phase, since the concentration based on the dry soil weight also showed an increase. In the two-week treatment (Fig. 10B), however, there was no such increase on a dry soil basis, so the high concentration in solution must have been due to moisture loss from that region.

The relatively low nitrate concentration in the unfrozen portion of the columns was probably due to denitrification. The decrease in nitrate concentration toward the warm end of the column could be attributed to a higher denitrification rate in the warmer portion of the column.

Nitrite concentration was low behind the freezing front (Fig. 10C and D), but it increased towards the warm end of the column. This could have been an indication that denitrification, which was probably low close to the freezing zone, increased with increasing temperature in the column. Also, a more rapid rate of denitrification in the warmer segments of the column could have created a concentration gradient along which nitrite could have diffused into the colder parts of the column. As the duration of the experiment was increased, nitrate loss in the warmer segments increased (Table 6), the concentration
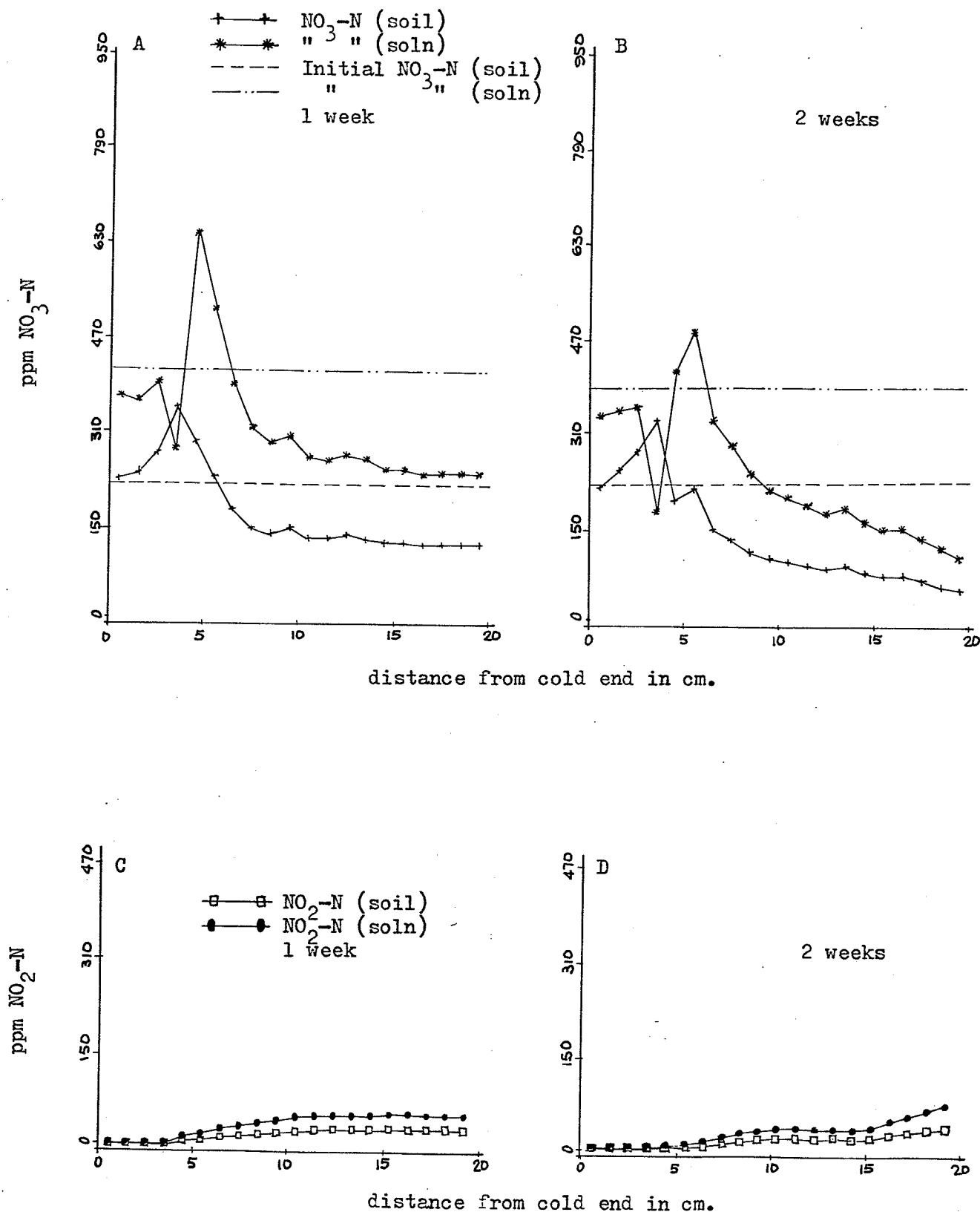
Fig. 10. Distribution of NO_3^- and NO_2^- in $Ca(NO_3)_2$-treated Red River soil columns after being subjected to the thermal gradient (initial moisture content = 54%).

gradient became more steep (Fig. 10B) and diffusion out of the cold soil probably increased.

Denitrification was important in the Red River soil at 54 percent moisture. The magnitude of the nitrogen loss at this moisture content made it impossible to separate biological effects from physical flux in the unfrozen portion of the soil columns.

The closed system had an unexpected effect on events taking place during the experiment. It affected soil aeration by allowing just a limited supply of oxygen and thus eventually providing conditions favourable for denitrification. From Tables 6 and 7 it can be seen that total nitrogen did not remain constant, but was sometimes much lower than the initial nitrogen concentration. This loss together with the accumulation of nitrite which was observed in Fig. 10 and in subsequent experiments provided evidence of denitrification having occurred in several of the columns.

The results obtained using $AgNO_3$ instead of $Ca(NO_3)_2$ in the Red River soil are shown in Fig. 11. After two weeks of exposure to the temperature gradient, there was some nitrogen and moisture loss from the column at the lower initial moisture content (Fig. 11A, Table 6). The decrease in nitrogen concentration on a soil basis but not on a solution basis (Table 6) may have been caused by a leak of liquid containing dissolved nitrate.

There was no evidence of nitrate transport to the colder soil similar to that observed in the $Ca(NO_3)_2$-treated column at 44 percent moisture (Fig. 9). The nitrate and moisture loss observed in the $AgNO_3$-treated column probably determined to some extent the nitrate

TABLE 6. EFFECT OF MOISTURE CONTENT AND LENGTH OF FREEZING PERIOD ON N RECOVERY IN RED RIVER SOIL

NO_3^- Source	Length of Freezing Period (wks)	Gravimetric Moisture Content		Total N on Dry Soil Basis (ppm)		Total N in Solution (ppm)	
		Initial	Final	Initial	Final	Initial	Final
Check	1	45.62	47.06	34.13	27.23	74.81	64.40
"	2	45.98	47.91	34.13	13.62	74.23	31.49
"	1	53.65	55.30	34.13	7.00	63.62	9.33
"	2	53.42	52.60	34.13	3.48	63.89	5.17
$Ca(NO_3)_2$	1	43.98	43.53	220.15	206.18	500.57	539.15
"	2	44.12	45.18	232.61	227.24	527.22	556.06
"	1	55.83	56.04	230.06	193.89	412.07	352.60
"	2	56.81	58.11	222.13	151.70	391.01	266.77
$AgNO_3$	2	45.35	41.67	194.60	170.49	429.11	428.91
"	2	53.58	54.93	195.04	198.01	364.02	375.74

TABLE 7. EFFECT OF MOISTURE CONTENT AND LENGTH OF FREEZING PERIOD ON N RECOVERY IN PORTAGE SOIL

| NO_3^- Source	Length of Freezing Period (wks)	Gravimetric Moisture Content		Total N on Dry Soil Basis (ppm)		Total N in Solution (ppm)	
		Initial	Final	Initial	Final	Initial	Final
Check	1	33.35	30.69	51.18	48.61	153.46	167.26
"	2	33.77	33.50	51.18	33.64	151.55	112.46
"	1	44.11	43.50	51.18	9.53	116.03	18.57
"	2	43.21	43.33	51.18	5.48	118.44	10.41
$Ca(NO_3)_2$	1	33.64	30.44	201.97	159.32	600.39	536.21
"	2	33.36	29.82	199.77	113.69	598.83	368.45
"	1	43.95	41.53	196.38	137.73	446.83	333.80
"	2	42.90	41.51	193.70	111.92	451.52	255.28
$AgNO_3$	2	33.24	35.11	180.18	203.01	542.06	593.17
"	2	42.98	42.90	187.95	157.30	437.30	370.86
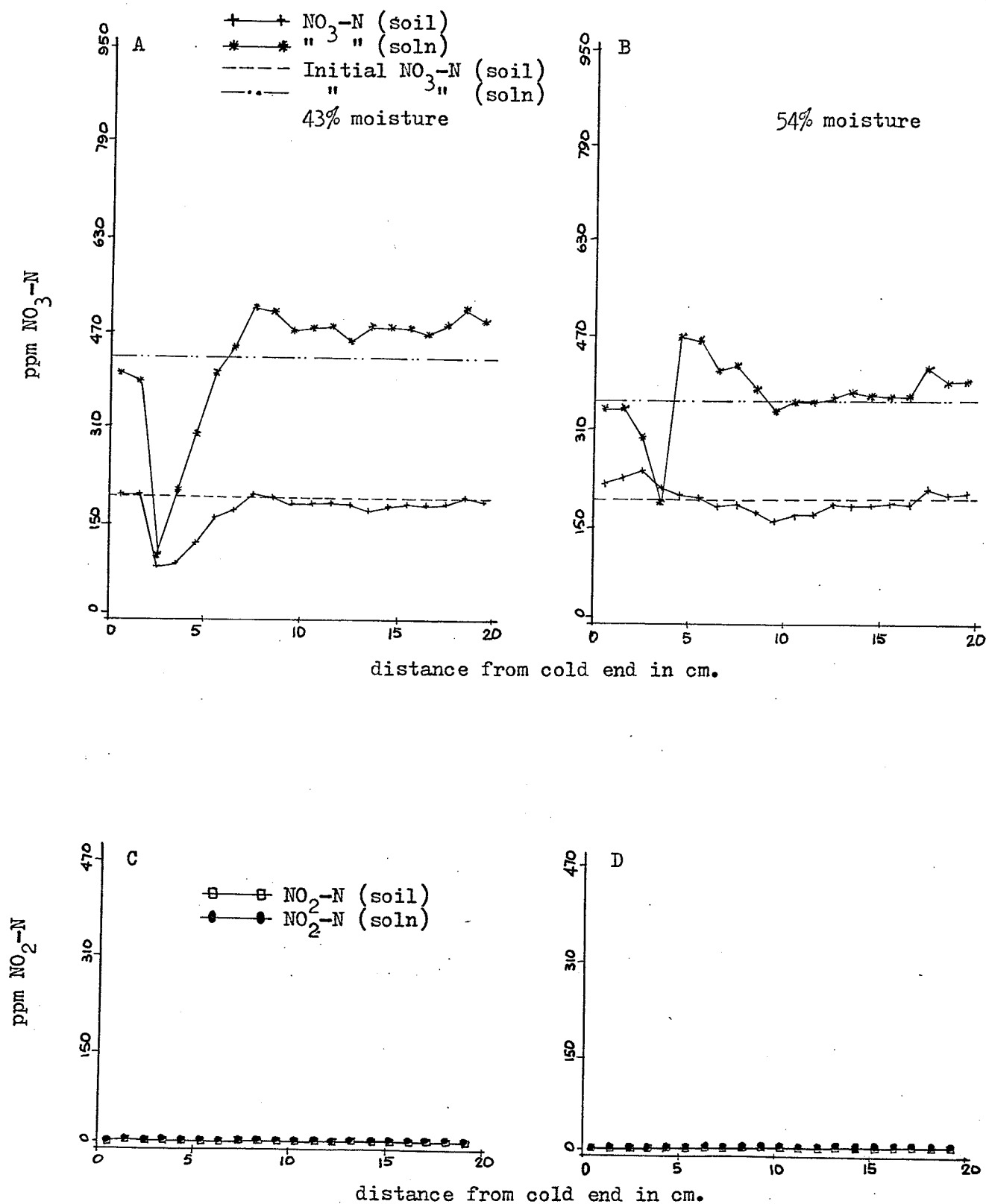
Fig. 11. Distribution of NO_3^- and NO_2^- in $AgNO_3$-treated Red River soil columns after being subjected to the thermal gradient for 2 weeks.

distribution in the soil.

Nitrate concentration in solution in the unfrozen zone was high despite low concentrations on a dry soil basis. This indicated that there was vapour transport to the frozen zone. However, there was no suggestion of liquid movement to the warm end as part of a circulatory flow of moisture.

At the higher moisture content (54%), there was no indication of denitrification having occurred in the $AgNO_3$-treated soil (Fig. 11B, Table 6). By comparison, nitrogen recovery in the $Ca(NO_3)_2$-treated column at a similar moisture content was low (Fig. 10B, Table 6). Evidently the silver ion had a toxic effect on the denitrifiers in the soil.

The nitrate distribution in Fig. 11B indicated nitrate transport to the frozen soil. This was not observed in a similarly treated column at a lower moisture content (Fig. 11A). A minimum in the solution concentration curve at the point of ice accumulation (4 cm) suggested that vapour transfer to that depth was in excess of liquid transfer. At lower depths, the high nitrate concentration in solution was similar to that observed in some previous columns (Fig. 9A and B, Fig. 11). An accumulation of nitrate in the warmer portion of the column showed that liquid moved toward the warm end of the column into a net evaporation sink.

Nitrate and nitrite distribution in the Portage soil columns initially at 33 percent moisture and treated with approximately 200 ppm $Ca(NO_3)_2$-N are shown in Fig. 12. The results obtained in the untreated soil columns are shown in the Appendix (Fig. A21).

Nitrate was transported to the frozen zone in both one-week and two-week treatments. The net increase in nitrate in the frozen zone was greater in the one-week treatment (Fig. 12A) than in the two-week treatment (Fig. 12B) but total nitrogen (nitrate and nitrite) was almost equal in the two. Unlike the Red River soil the depth of maximum nitrate concentration on a dry soil basis in the Portage soil did not coincide with the depth of maximum moisture content.

Outside the frozen zone, nitrate concentration on a soil as well as solution basis was high. This suggested either nitrate exclusion from the ice phase or vapour transfer to the freezing soil.

Nitrogen loss through denitrification was high in both one-week and two-week cold treatments. However, this loss was greater in the two-week treatment (Fig. 12, Table 7). The nitrite distribution curves (Fig. 12C and D) showed an accumulation of nitrite at both the cold and warm ends of the column. The relatively high nitrite concentration in the frozen soil could be attributed partly to biological activity prior to freezing and partly to transport from lower depths.

Fig. 13 shows the nitrate and nitrite distribution in $Ca(NO_3)_2$-treated Portage soil columns after one week and two weeks of exposure to the temperature gradient at an initial moisture content of 44 percent. Nitrate and nitrite distribution in untreated soil columns at the same moisture content are shown in the Appendix (Fig. A22). The distribution of nitrate in the two columns suggests that both moisture transport and denitrification were contributing factors in determining the shape of the distribution curve.
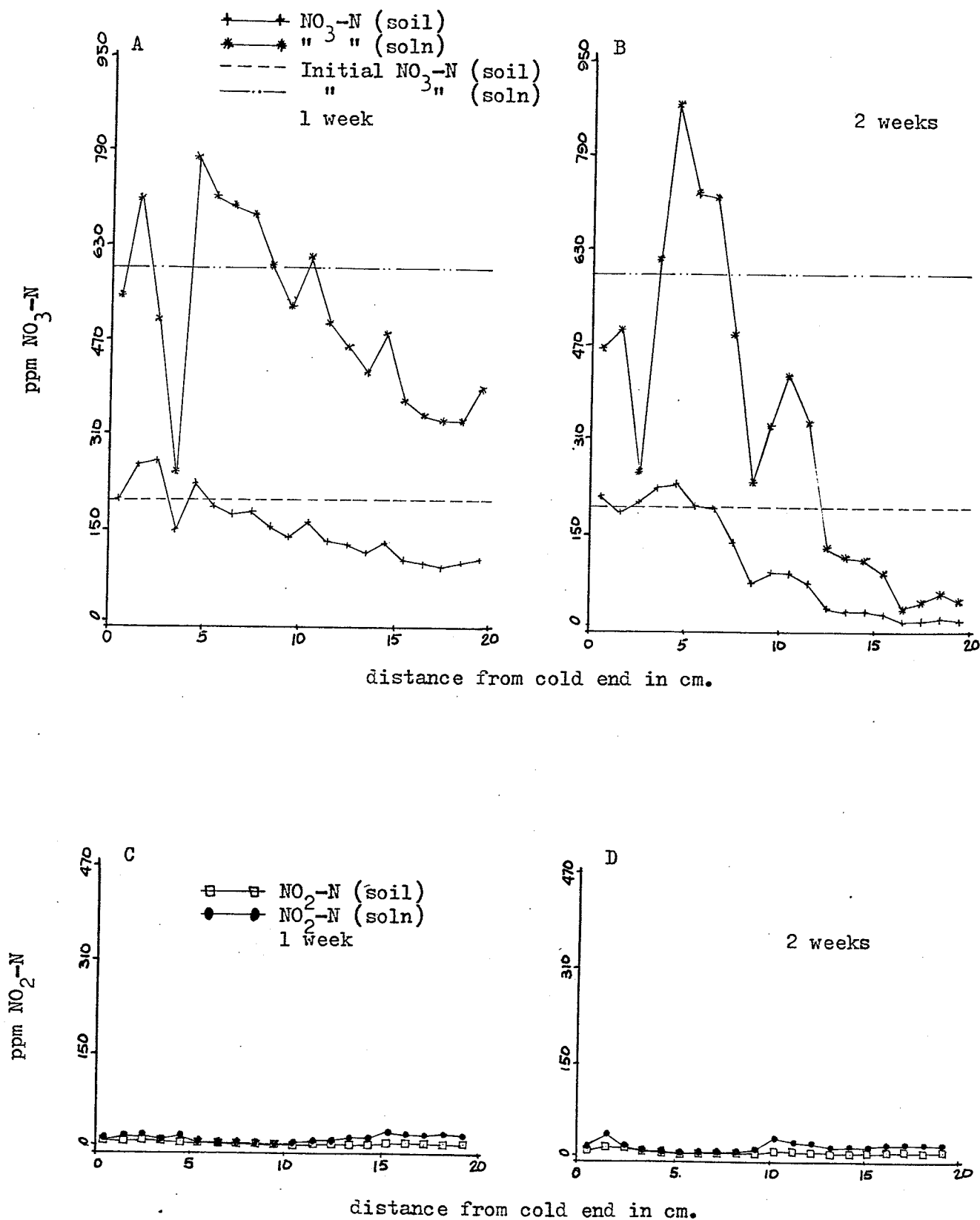
Fig. 12. Distribution of NO_3^- and NO_2^- in $Ca(NO_3)_2$-treated Portage soil columns after being subjected to the thermal gradient (initial moisture content = 33%).
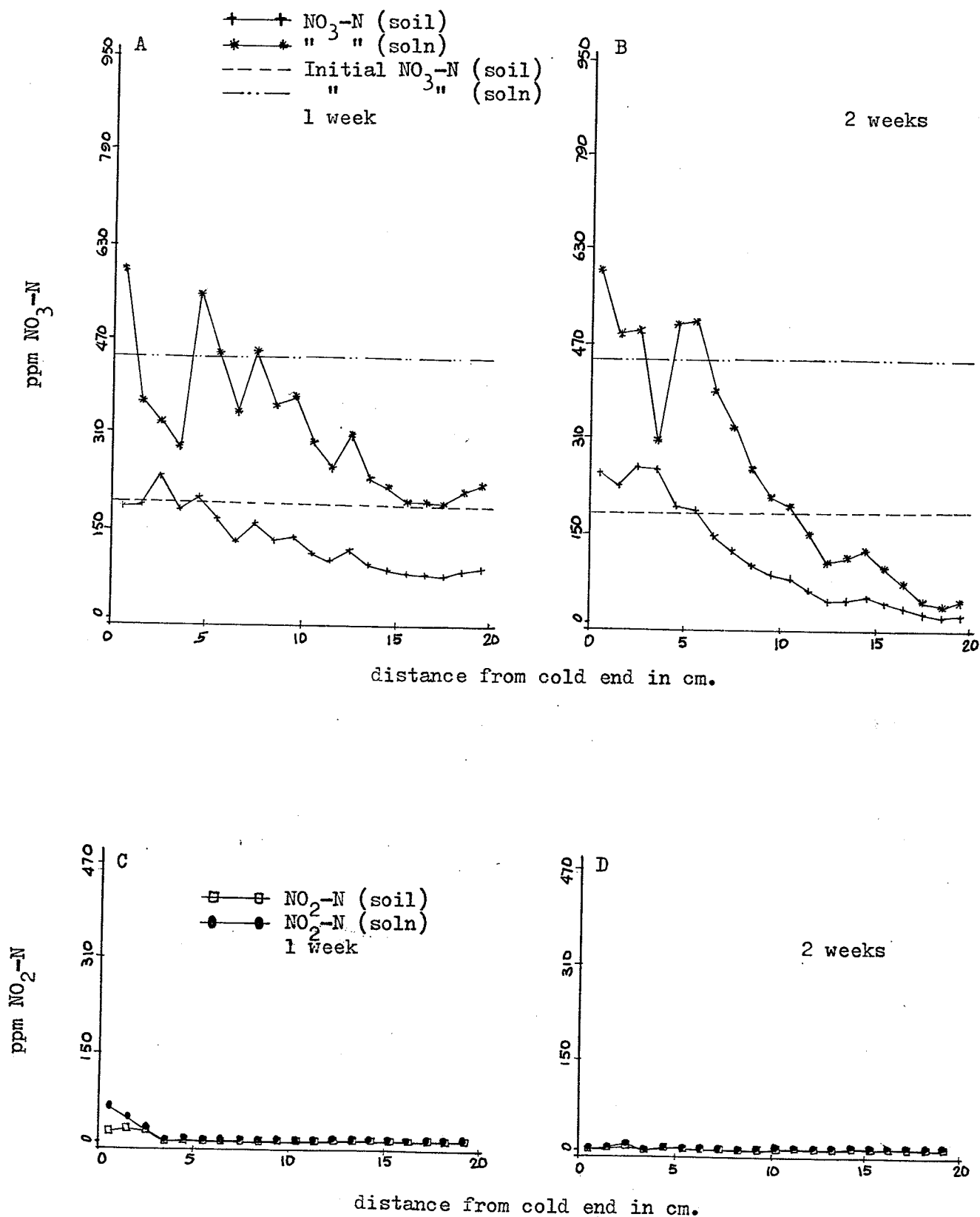
Fig. 13. Distribution of NO_3^- and NO_2^- in $Ca(NO_3)_2$-treated Portage soil columns after being subjected to the thermal gradient (initial moisture content = 44%).

Both treatments showed a net transfer of nitrogen to the colder region of the column. The low solution concentration at the ice front (Fig. 13A and B) suggested a high proportion of moisture transport in the vapour form.

Nitrate distribution in the warmer portion of the columns was greatly affected by denitrification. Thus it did not provide information about the relative importance of liquid and vapour transfer.

A comparison of the nitrite distribution in the two columns (Fig. 13C and D) showed a higher nitrite concentration in the frozen zone of the one-week treatment. The time required to freeze up to the 3 cm depth was found to be around one day, and it is doubtful whether so much nitrite could have been produced in that region before it was frozen. Thus this introduces the possibility that nitrite produced in the warmer region diffused into the frozen layer before the ice front became impermeable to the dissolved ions.

Nitrate and nitrite distribution in the Portage soil columns treated with $AgNO_3$ are shown in Fig. 14. Denitrification was effectively, though not totally prevented by the silver ion at the lower moisture content. However, at the higher moisture content nitrogen loss through denitrification was high (Fig. 14).

Nitrate concentration based on the dry soil weight was high in the frozen zone of the 33 percent moisture treatment (Fig. 14A), indicating that nitrate was transported there in solution. However, it can be inferred from the low concentration in solution that moisture was transferred in the vapour phase as well, thus causing a
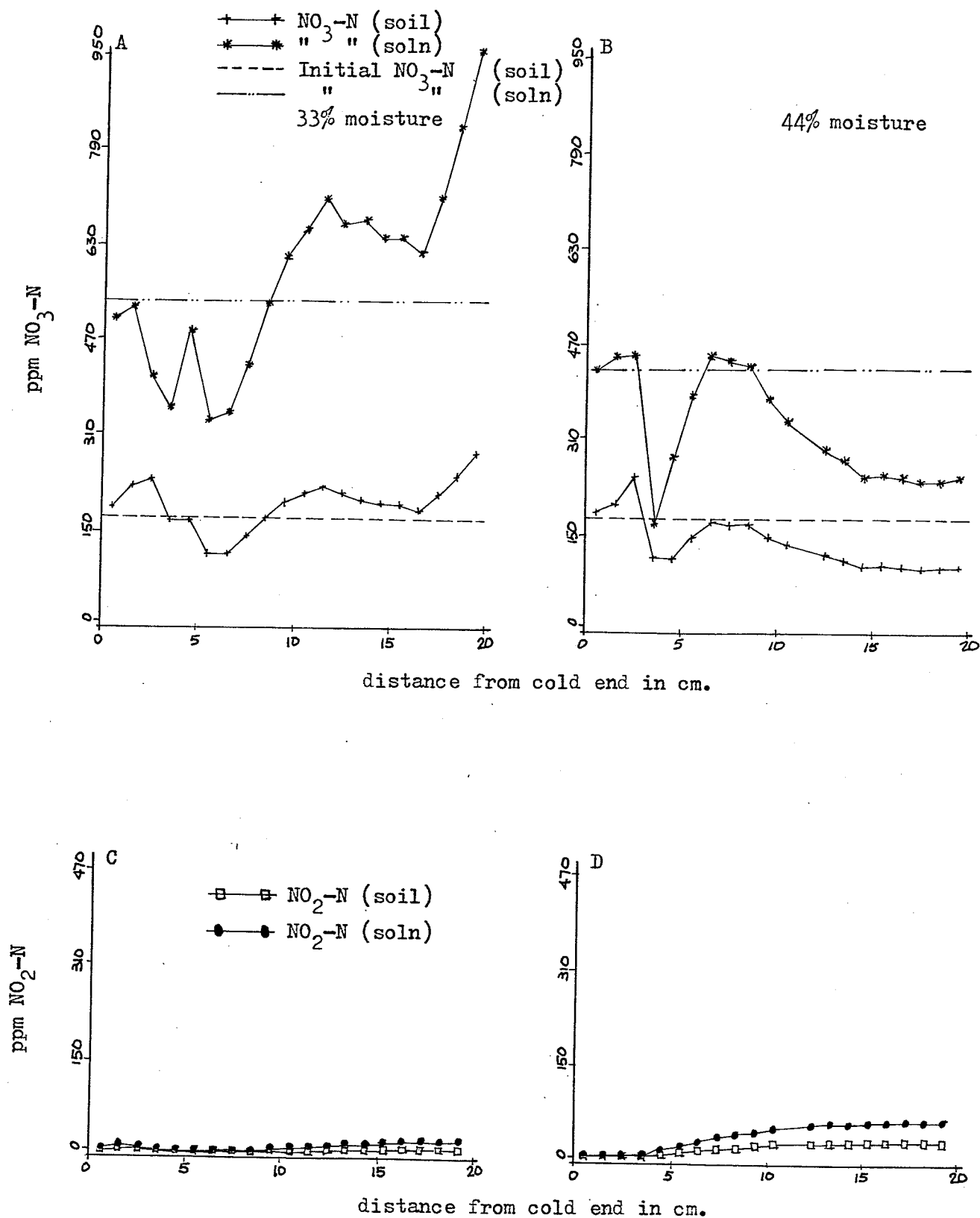
Fig. 14. Distribution of NO_3^- and NO_2^- in $AgNO_3$-treated Portage
soil columns after being subjected to the thermal gradient
for 2 weeks

dilution of the soil solution.

In the unfrozen soil, after an initial decrease beyond the ice front, there was a gradual increase in the nitrate concentration with depth, indicating that there was internal circulation of moisture.

At the higher moisture content (44%), nitrate concentration in the frozen portion of the column indicated liquid flow into the frozen soil, and vapour condensation at the freezing front. In the unfrozen portion of the column, however, nitrate transport was obscured by denitrification.

The nitrite distribution curves showed an increase in nitrite concentration toward the warmer end of the column (Fig. 14C and D). There was some nitrite in the frozen zone of the column at 33 percent initial moisture content (Fig. 14C). However, there was no evidence of denitrification in the frozen zone or nitrate transport to that zone in the 44 percent moisture treatment, despite higher nitrite levels in the unfrozen soil (Fig. 14D).

Nitrate distribution in the untreated Red River and Portage soil columns showed some of the characteristics observed in the treated soils (Fig. A19 to A22). There were indications of both liquid and vapour flow toward the cold soil in these columns. However, because of low nitrate concentration in the untreated soil, changes resulting from the application of the thermal gradient were not as obvious as in the treated soil.

In both the Red River and Portage soils, the nitrate ion acting as a tracer served to distinguish between liquid and vapour movement. There was generally a net movement of nitrate to the cold

soil, which was also the direction of net movement of moisture. Since the transport of nitrate was assumed to have been due to transport by water in the liquid phase, the results would suggest that liquid flow occurred toward the cold portion of the columns. While a net increase in nitrate concentration on a soil basis was used as an indicator of liquid movement to the cold zone of the column, a dilution of the nitrate concentration in solution in that region served to indicate that there was also transport of water to the frozen soil in the vapour phase. Generally a plot of the distribution of nitrate concentration in solution at different depths showed a minimum at the ice front. This dilution was assumed to be due to the retention of condensed vapours as ice. The transfer of vapour away from the unfrozen soil resulted in a concentration of the solution in the unfrozen portion where nitrate concentration on a soil basis was equal to or even lower than what it was before being subjected to the temperature gradient.

The accumulation of NO_3^- at the warm end based on both soil and solution concentration was taken as evidence of internal convection of liquid resulting from the condensation of vapour in the cold soil, and its subsequent return as a liquid after a favourable potential had been established. This was evident in the columns where there was no denitrification.

The magnitude of the net nitrate flux in the $Ca(NO_3)_2$-treated Red River soil increased with an increase in the moisture content of the soil. This effect was observed in the experiments of one-week as well as those of two-week duration. The moisture content, however,

had a twofold effect on the nitrate distribution in the soil. It affected the amount of nitrate transported to the frozen soil as well as the amount of nitrate lost through denitrification. Such losses were less in the Red River soil and thus the effect of moisture content on the transport of nitrate was more obvious. In similarly treated Portage soil columns the effect of moisture content on nitrate movement was obscured by denitrification.

Denitrifying activity was greater in the Portage soil than in the Red River soil, so total nitrogen recovery was less. This could have been due to the higher organic matter content of the Portage soil. A high organic matter content is expected to promote a more rapid denitrification through two effects on the soil microflora. It influences the biological oxygen demand and secondly it furnishes energy for the growth of the denitrifying bacteria and serves as a hydrogen donor for the denitrifying process.

Nitrite accumulated in the $Ca(NO_3)_2$-treated Red River soil at the higher moisture content but not at the lower moisture content. In similarly treated Portage soil columns nitrite levels were higher at the lower moisture content.

The duration of the cold treatment did not affect nitrate accumulation in the frozen soil at any given moisture content. Its effect on the internal liquid circulation and nitrate accumulation at the warm end was apparent in the Red River soil at the lower moisture content. In these columns increasing the duration of the experiment resulted in increased nitrate accumulation at the warm end. In the other columns there might also have been a similar

effect on liquid transport to the warm end. However, this was not indicated by nitrate distribution in the soil because nitrate was depleted through denitrification at the same time as its transfer in the liquid.

Substitution of $Ca(NO_3)_2$ with $AgNO_3$ indicated that the silver ion retarded but did not totally eliminate the denitrification process in either soil. Denitrification was significant in the Portage soil at the higher moisture content.

The results obtained with the $AgNO_3$-treated soils were different from those obtained in the $Ca(NO_3)_2$-treated soil. Moisture movement was found to be greater in the $Ca(NO_3)_2$-treated than in the $AgNO_3$ treated soil. It was also found that ion distribution was different.

SUMMARY AND CONCLUSIONS

The downward movement of nitrogen from three surface-applied nitrogen fertilizers was followed in two Manitoba soils. Calcium nitrate, urea and ammonium sulphate were applied at the rate of 500 lb N per acre to a Red River clay and a Portage loam, and the distribution of nitrogen determined at intervals over an eighteen week period. This provided information about the extent of nitrogen penetration into the field during a period comparable to a growing season in Manitoba.

Nitrogen movement was found to be determined by climatic conditions and by soil characteristics. Nitrate from $Ca(NO_3)_2$ applied in the spring moved downward in the soil profile. This movement was greater in the Portage loam than in the Red River clay. Nitrate was rather immobile in the soil for most of the summer period, probably due to evaporative loss of water from the soil surface. Upward movement was detected at both sites during dry periods. In the fall nitrate penetrated to lower depths since rainfall was higher and evaporation was low. The position of maximum concentration of nitrate was transferred from the surface to the 9 or 12 inch depth.

Ammonium nitrogen from urea and $(NH_4)_2SO_4$ was retained within 9 or 12 inches of the point of application. The movement of nitrogen in these plots was less than in the $Ca(NO_3)_2$ plots. Movement of nitrogen depended on the rate of nitrification which was relatively slow in both soils. The depth of penetration of nitrate was small during the early stages of the field experiment, but it increased

as the ratio of NO_3^- to NH_4^+ increased. Depths of penetration were greater in the Portage soil where the rate of nitrification was more rapid than in the Red River soil.

The rate of nitrification in the Portage soil (pH 8.2) was more rapid with $(NH_4)_2SO_4$ than with urea. The reverse was true for the Red River soil (pH 6.5) where almost 55 percent of the total N in the $(NH_4)_2SO_4$ plot was still in the NH_4^+ form on October 8, 1971 - 18 weeks after application.

The decrease in total nitrogen which occurred on all the plots was more marked in the Red River soil than in the Portage soil. This decrease was probably due to denitrification and immobilization.

It was concluded from this field experiment that even in the absence of a crop - a condition which should favour nitrate accumulation in the subsoil - there was no real evidence of nitrogen being easily moved downward during the summer period.

Chloride was applied to the soil to serve as a tracer of water moving through the soil profile. However, the initially high chloride levels in the soil made $CaCl_2$ applied at the rate of 500 lb Cl^- per acre ineffective as a tracer of water movement.

The Portage field experiment was terminated in October 1971, but samples were taken from the Red River soil in the spring and fall of the following year. The amount of nitrogen recovered in the spring sample was lower than that found in previous samples. There was also an apparent upward movement of nitrogen. It was then decided, as a result of these two findings, to simulate winter conditions in the laboratory.

Column studies were carried out in order to investigate some of the transport phenomena that accompany the freezing process in the soil. However, a study of the thawing process which is of equal interest and importance was not carried out.

An external temperature gradient of 1.5C/cm (-1OC to 2OC for a column 20 cm in length) was applied in each column study. Two initial moisture contents, one around field capacity and the other slightly higher, and two nitrogen compounds, $Ca(NO_3)_2$ and $AgNO_3$, were chosen.

The moisture distribution curves showed an accumulation of ice at the freezing front of both Red River and Portage soil columns. The ice formed in the Red River soil was of a dense nature and greater in magnitude than the porous type of frost formed in the Portage soil. The ice front penetrated to either the 4 cm or 5 cm depth and remained stationary at that depth during both one week and two weeks periods of the experiment. There was no apparent relationship between the moisture content and depth of ice penetration.

The effect of initial water content on moisture distribution was observed only in the Red River soil columns. The wetter soil columns showed a gradient of moisture content in the unfrozen soil which was not present in the drier soil columns. Ice accumulation in the frozen zone appeared to be less at higher than at lower moisture content, and the percentage of moisture transferred from the unfrozen to the frozen zone was also smaller.

There was increased transport of moisture to the cold side with an increase in the duration of the cold treatment in the Portage soil at 33 percent initial moisture content. Such an effect was

not observed in the soil columns at higher moisture content. In the Red River soil on the other hand, an increase in the duration of the cold treatment resulted in increased moisture transfer to the cold end of the wetter but not of the drier soil columns.

Different electrolytes in the soil were found to affect the magnitude of moisture movement. In both soils net moisture transfer in $AgNO_3$-treated columns was less than in either $Ca(NO_3)_2$-treated or untreated soil columns.

There was evidence of both liquid and vapour transport to the frozen portion of the columns. High nitrate concentration based on soil weight in the frozen zone indicated liquid transfer to that zone, while a dilution of the nitrate concentration in solution indicated vapour transport. This dilution was greatest at the point of maximum ice accumulation, indicating that the contribution of vapour transport was in excess of that of liquid transport.

Nitrate and liquid transport in the Red River soil were greater at the higher than at the lower moisture content. Such an effect was not observed in the Portage soil columns where NO_3^- was depleted through denitrification at the higher moisture content.

Internal convection of liquid was demonstrated in some columns where denitrification was minimal or absent. In these columns the condensation of vapour moving toward the cold end and its subsequent return along a liquid gradient to the warm end resulted in an accumulation of nitrate at the warm end of the column.

There were changes in nitrate content which were clearly due to denitrification, and which were related to the moisture content of the soils. Losses of nitrogen were greater at the higher moisture content

in both soils, but of a much greater magnitude in the Portage than in the Red River soil. The use of $AgNO_3$ reduced the rate of denitrification, but did not completely inhibit the process.

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APPENDIX
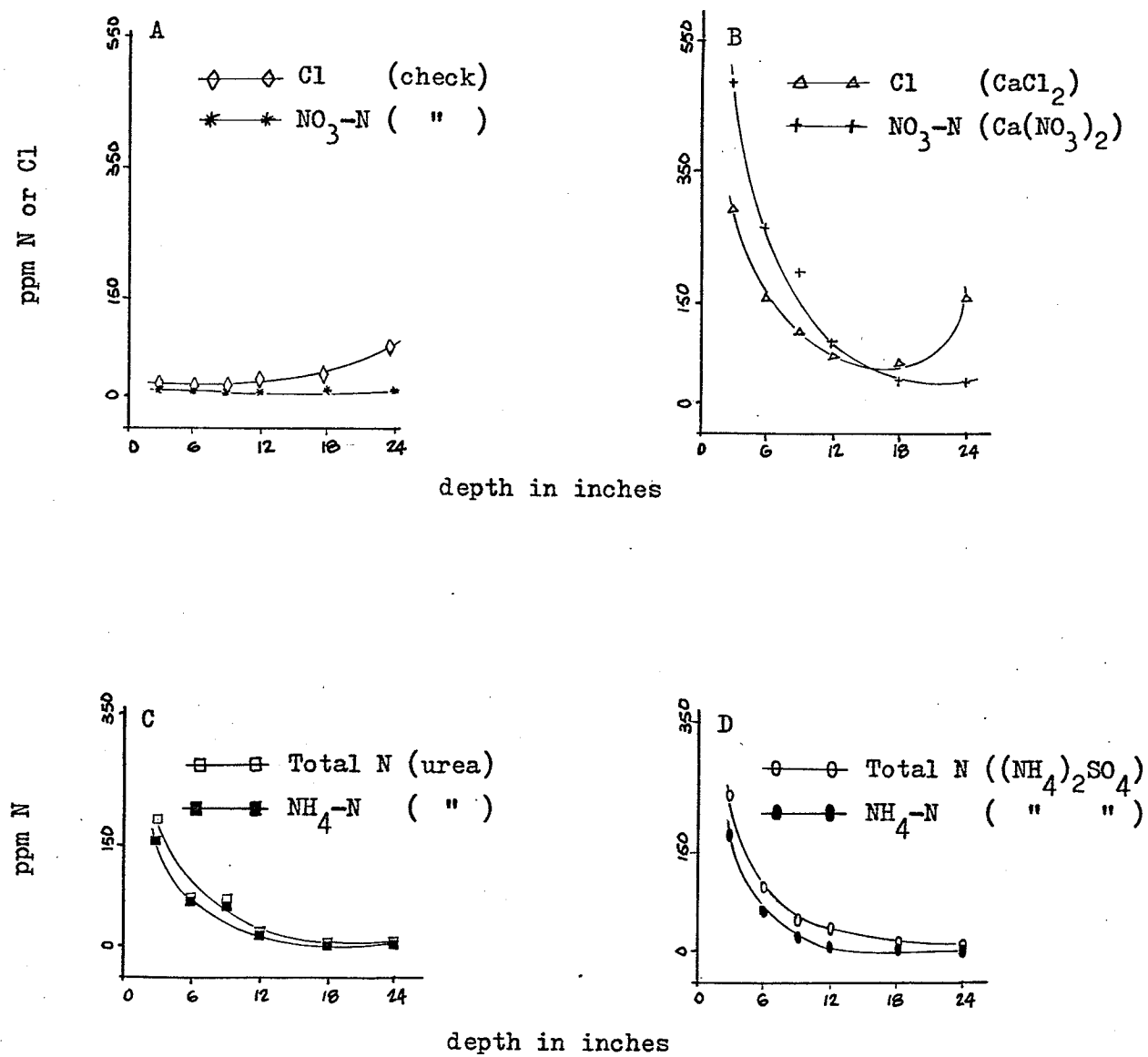
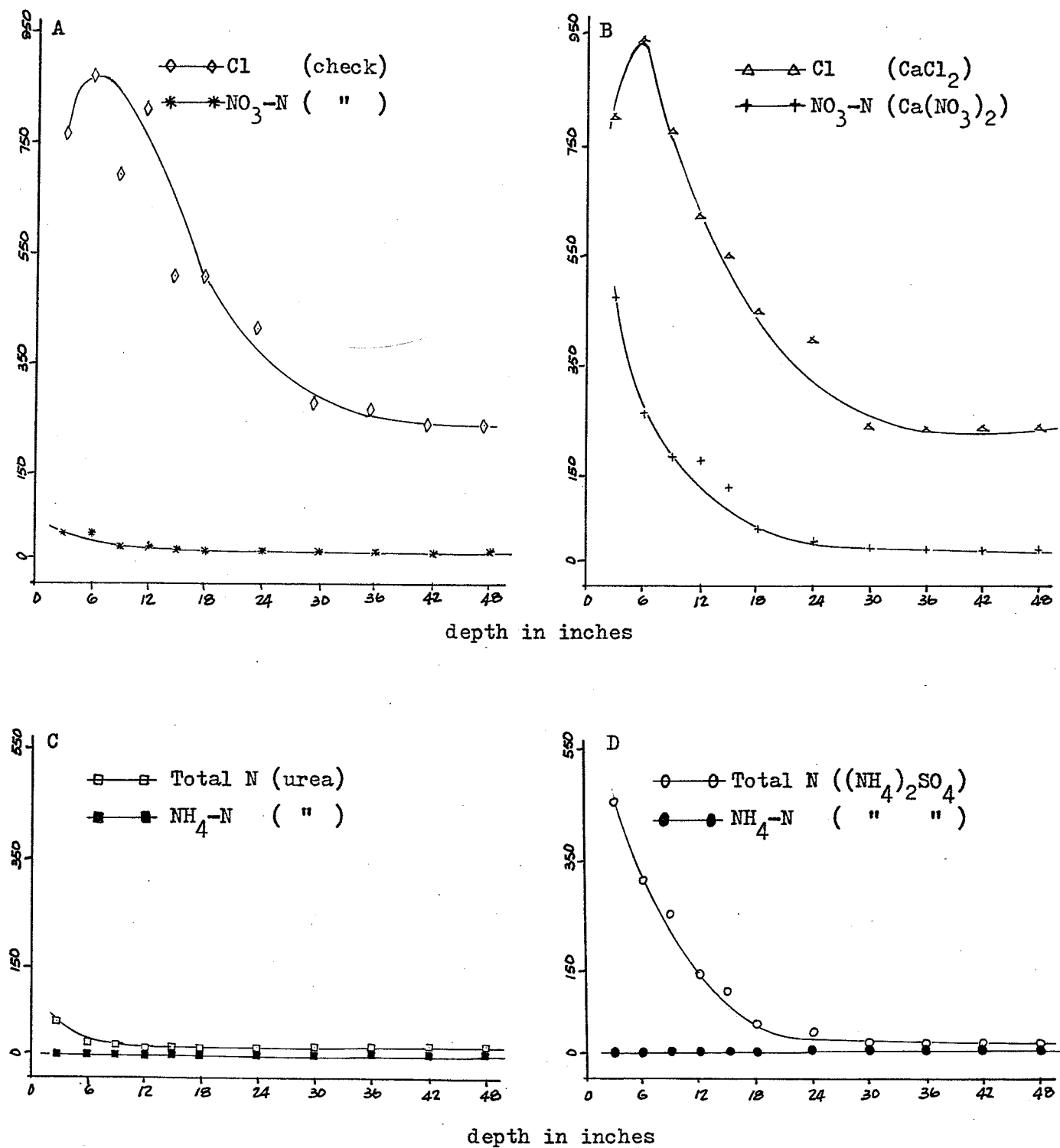Fig. A1. Nitrogen and chloride distribution in the Red River clay on June 15, 1971.
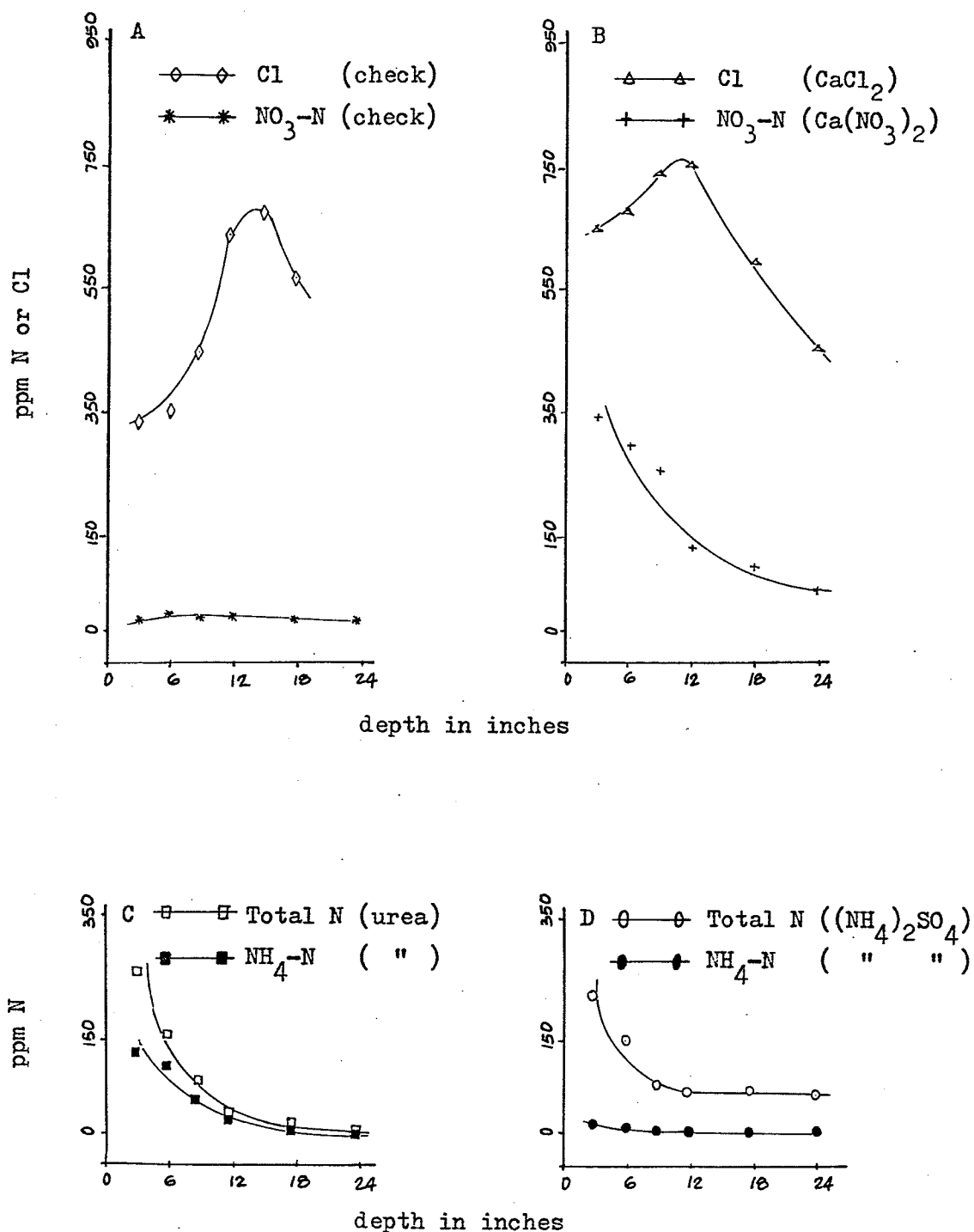
Fig. A2. Nitrogen and chloride distribution in the Portage loam on June 17, 1971.
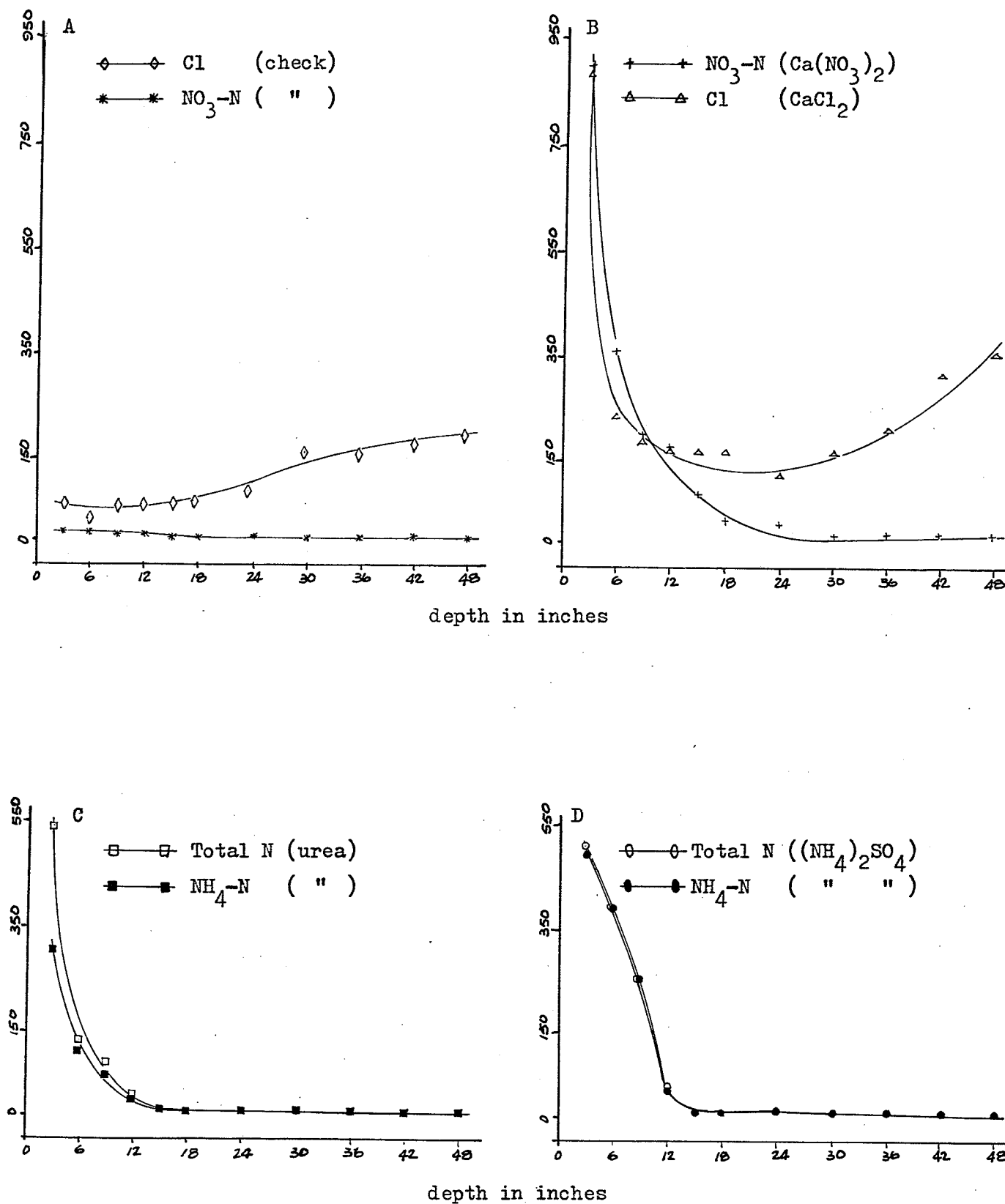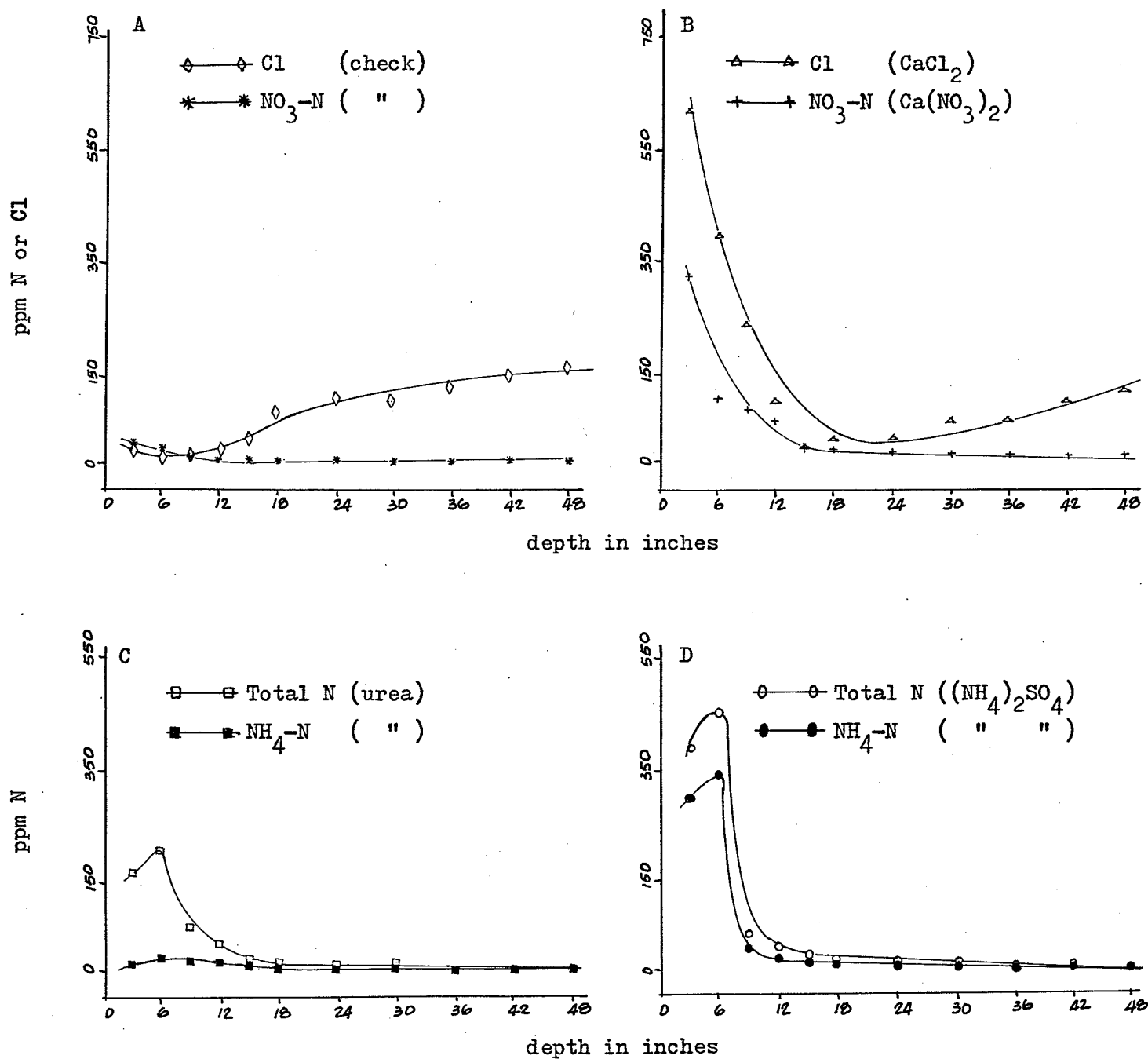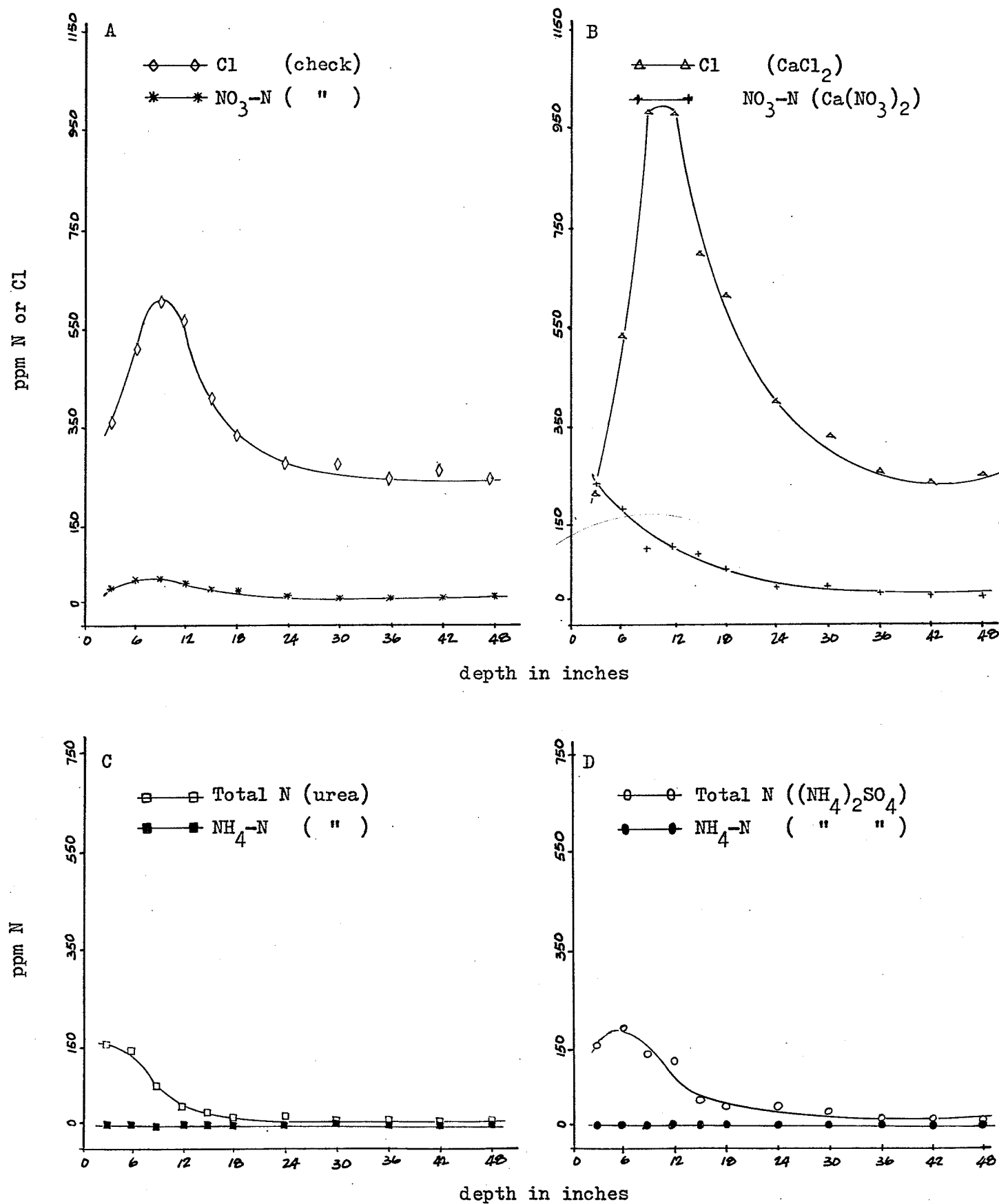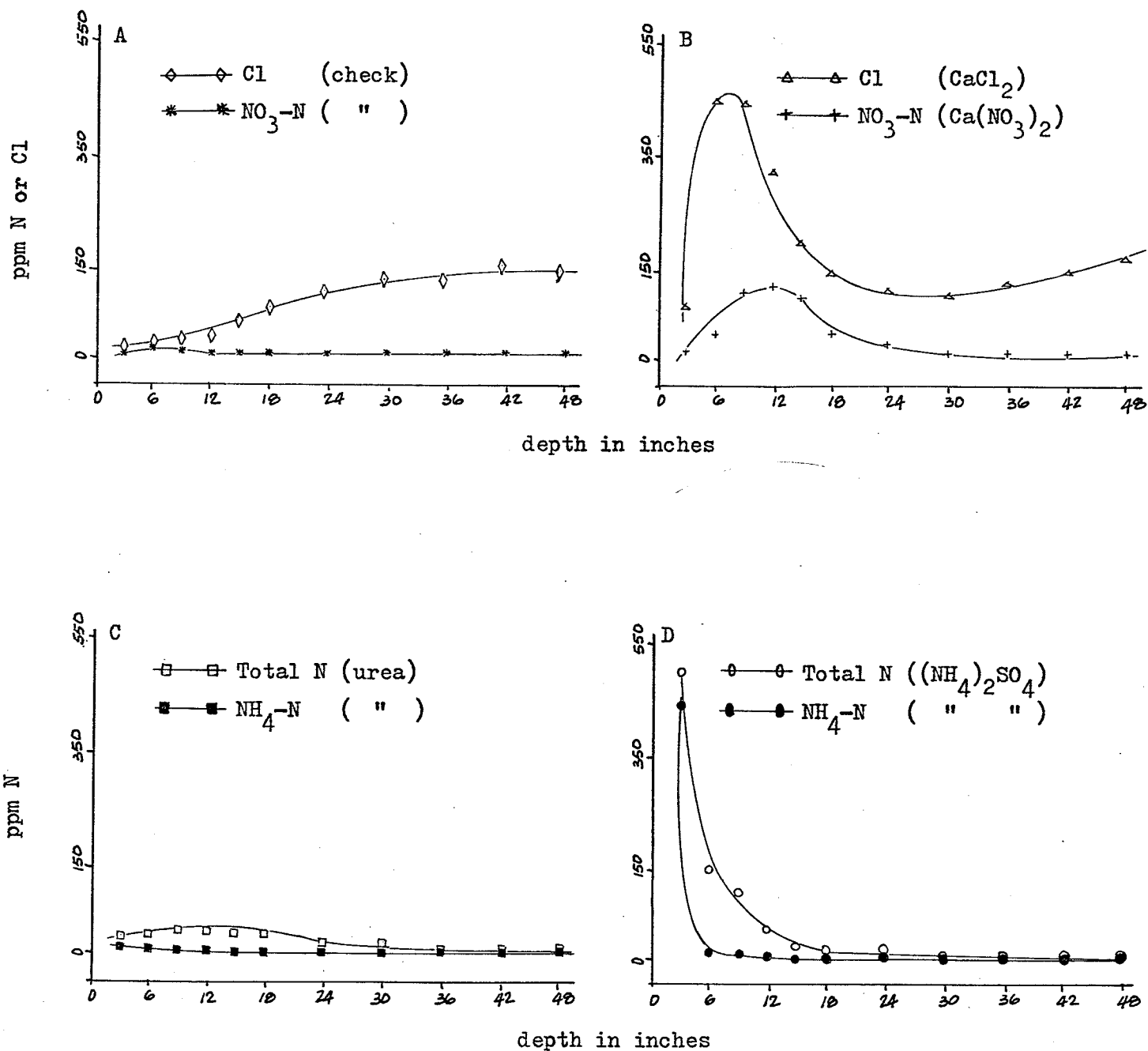
Fig. A3. Nitrogen and chloride distribution in the Red River
clay on June 29, 1971.

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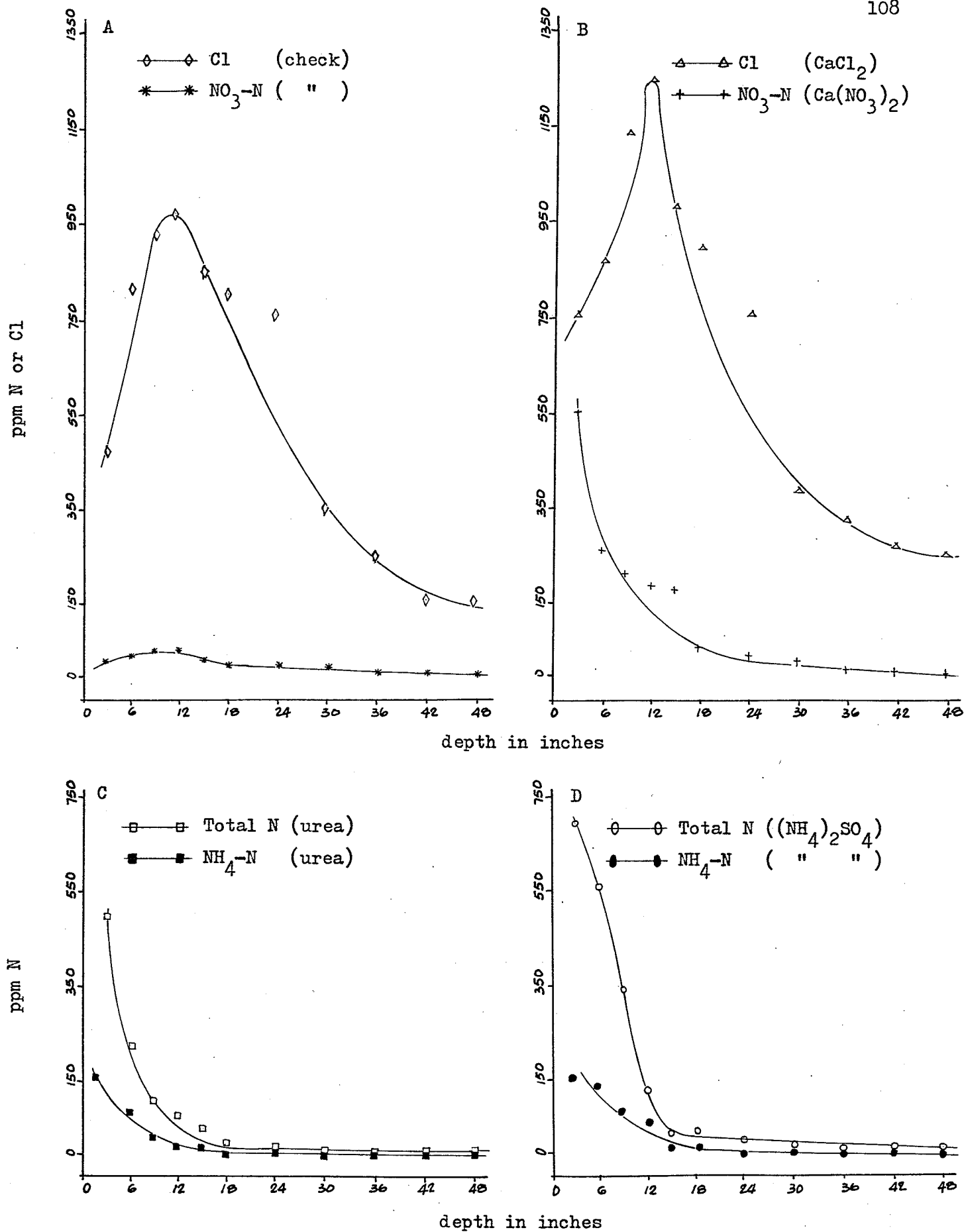
Fig. A4. Nitrogen and chloride distribution in the Portage loam
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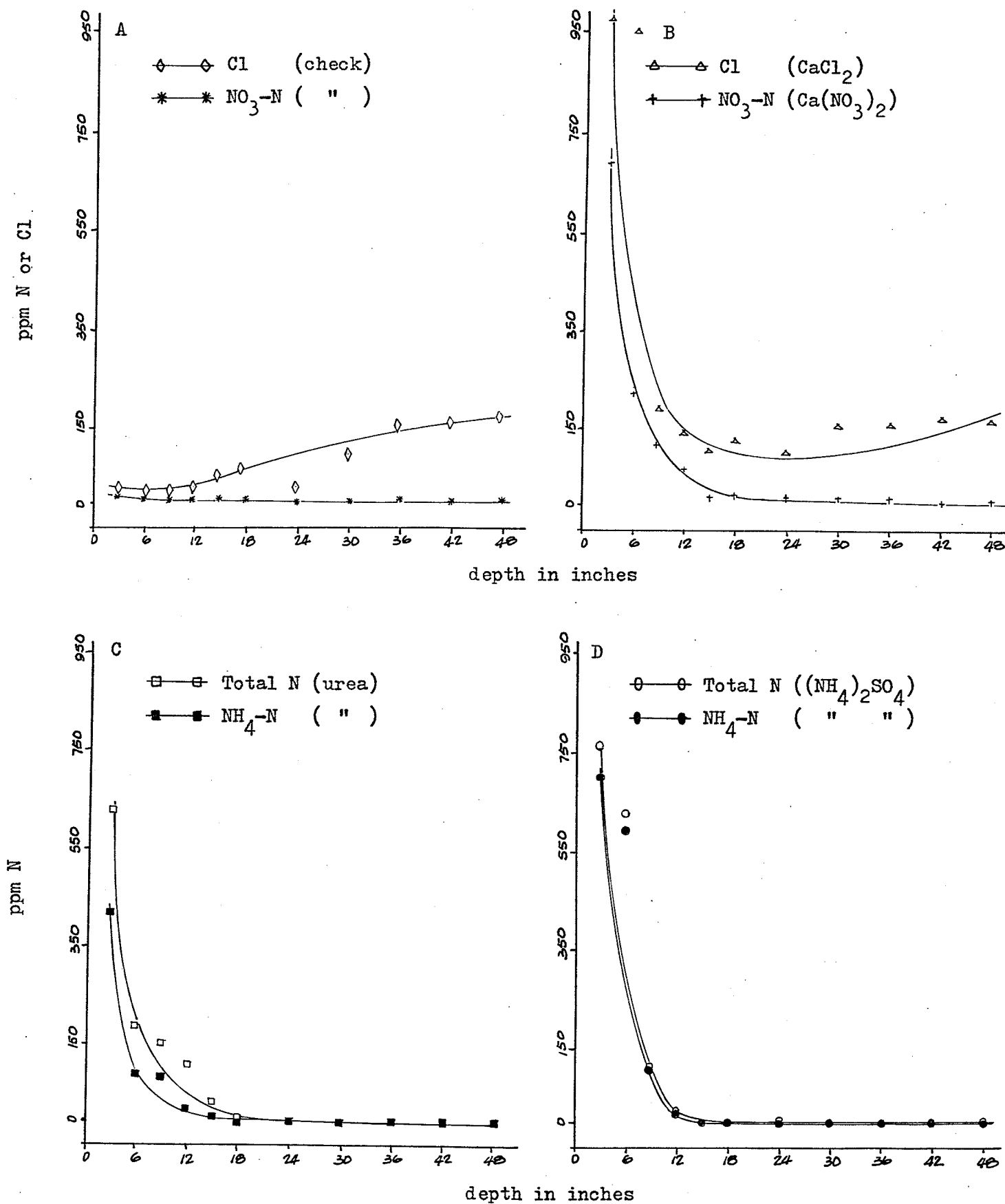
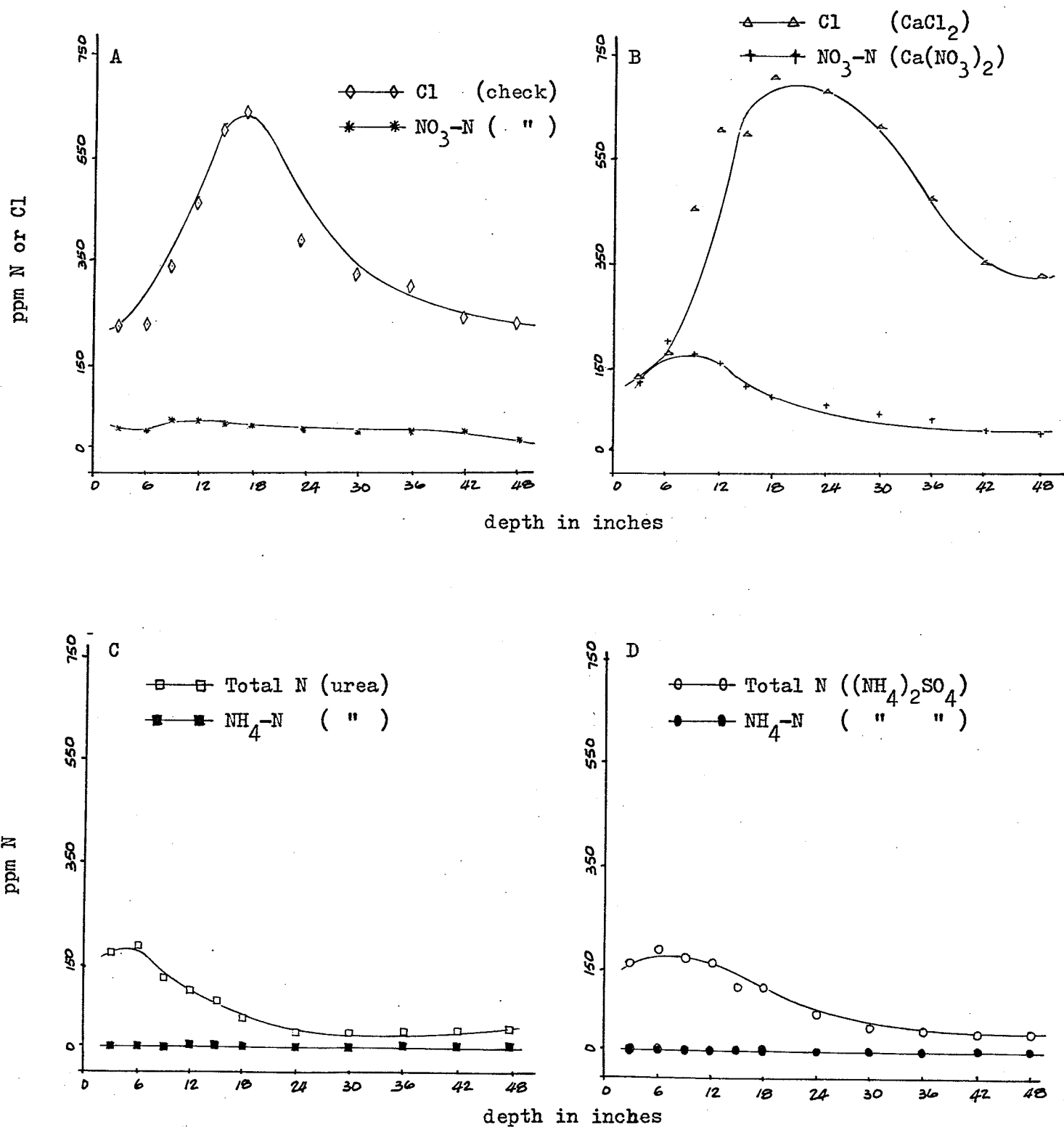Fig. A5. Nitrogen and chloride distribution in the Red River
clay on July 13, 1971.
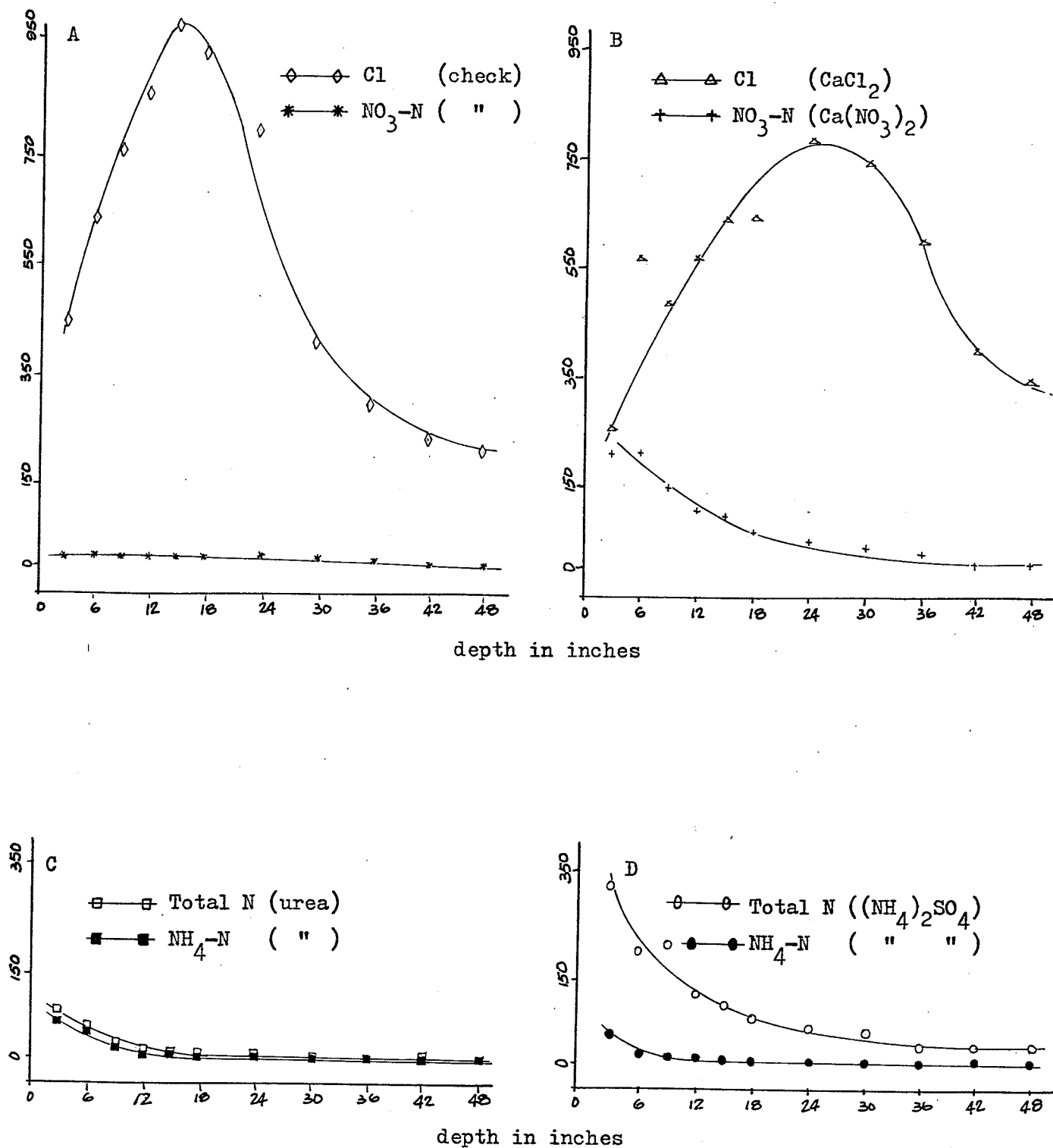
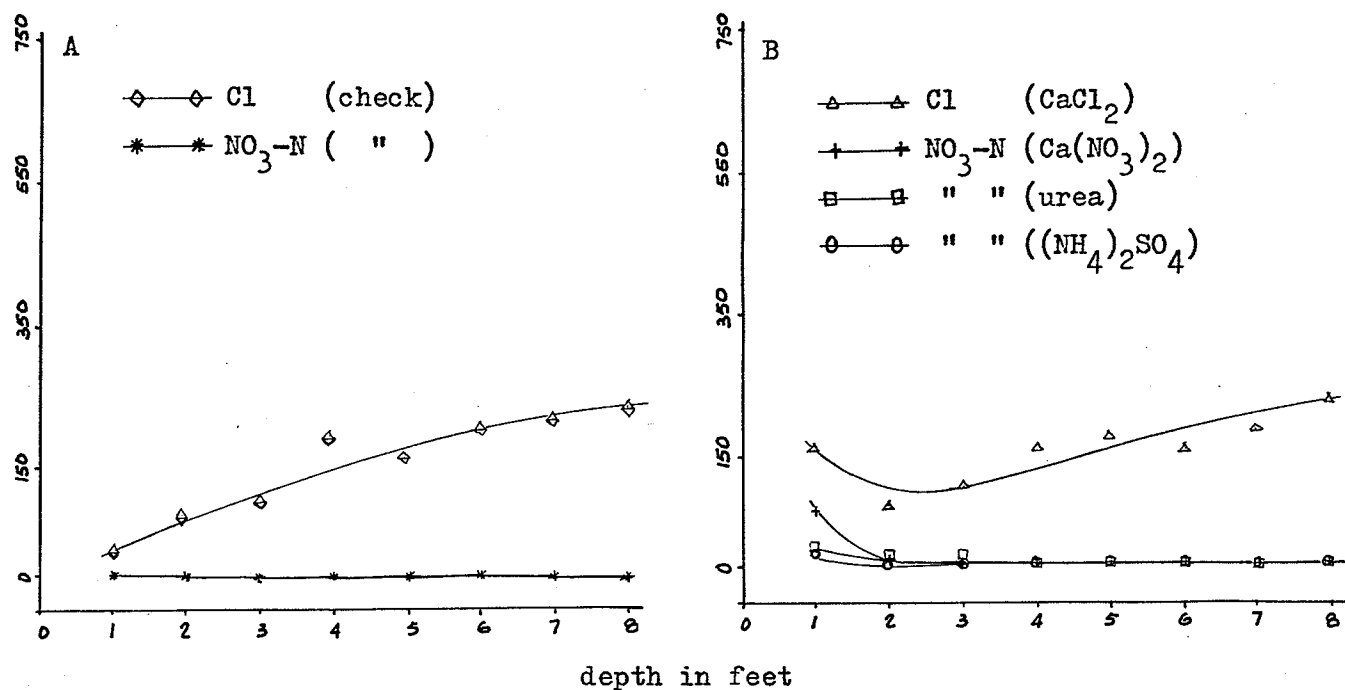Fig. A6. Nitrogen and chloride distribution in the Portage loam on July 15, 1971.
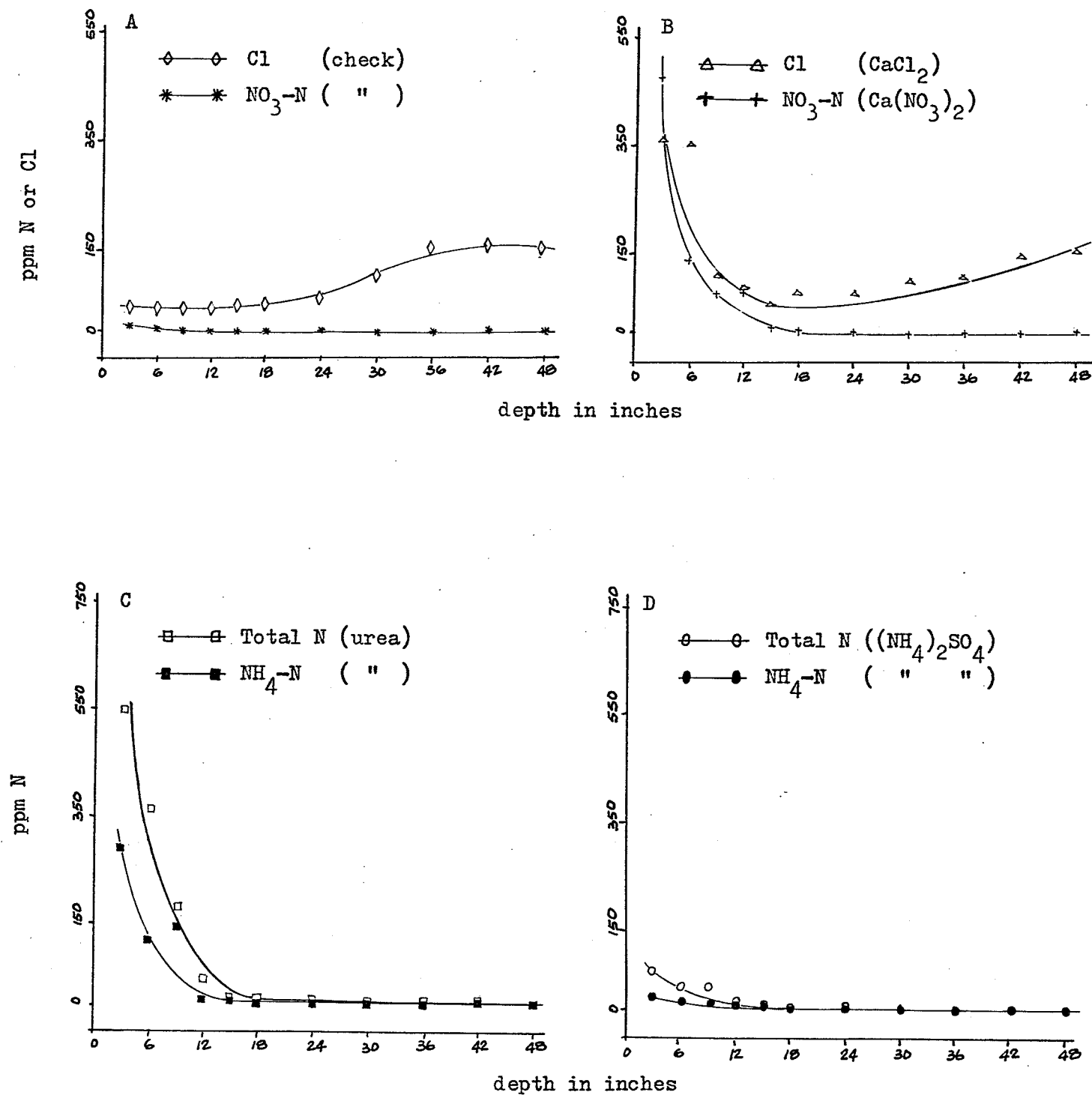
Fig. A7. Nitrogen and chloride distribution in the Red River
clay on July 29, 1971.
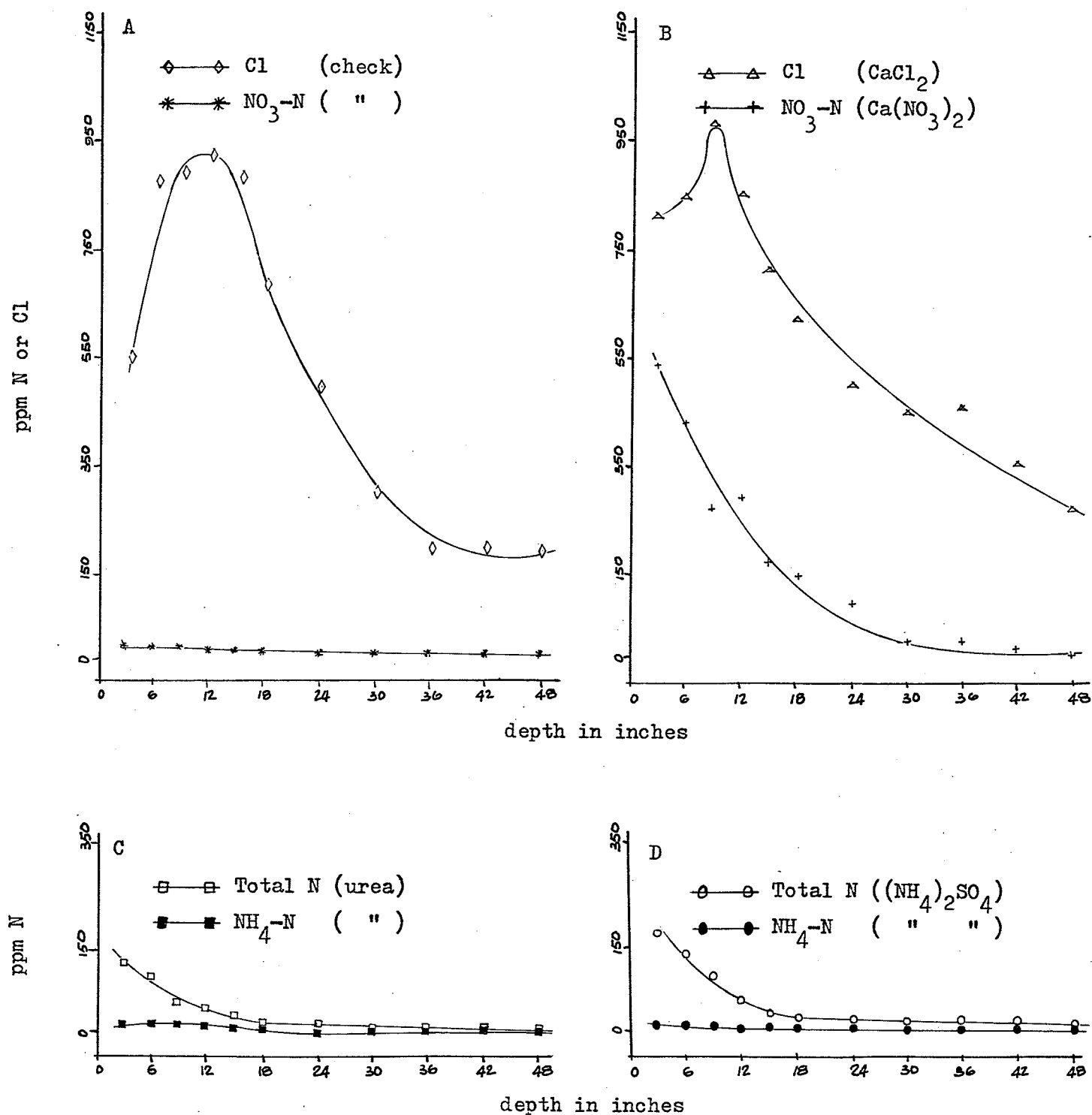
Fig. A8. Nitrogen and chloride distribution in the Portage loam
on July 31, 1971.
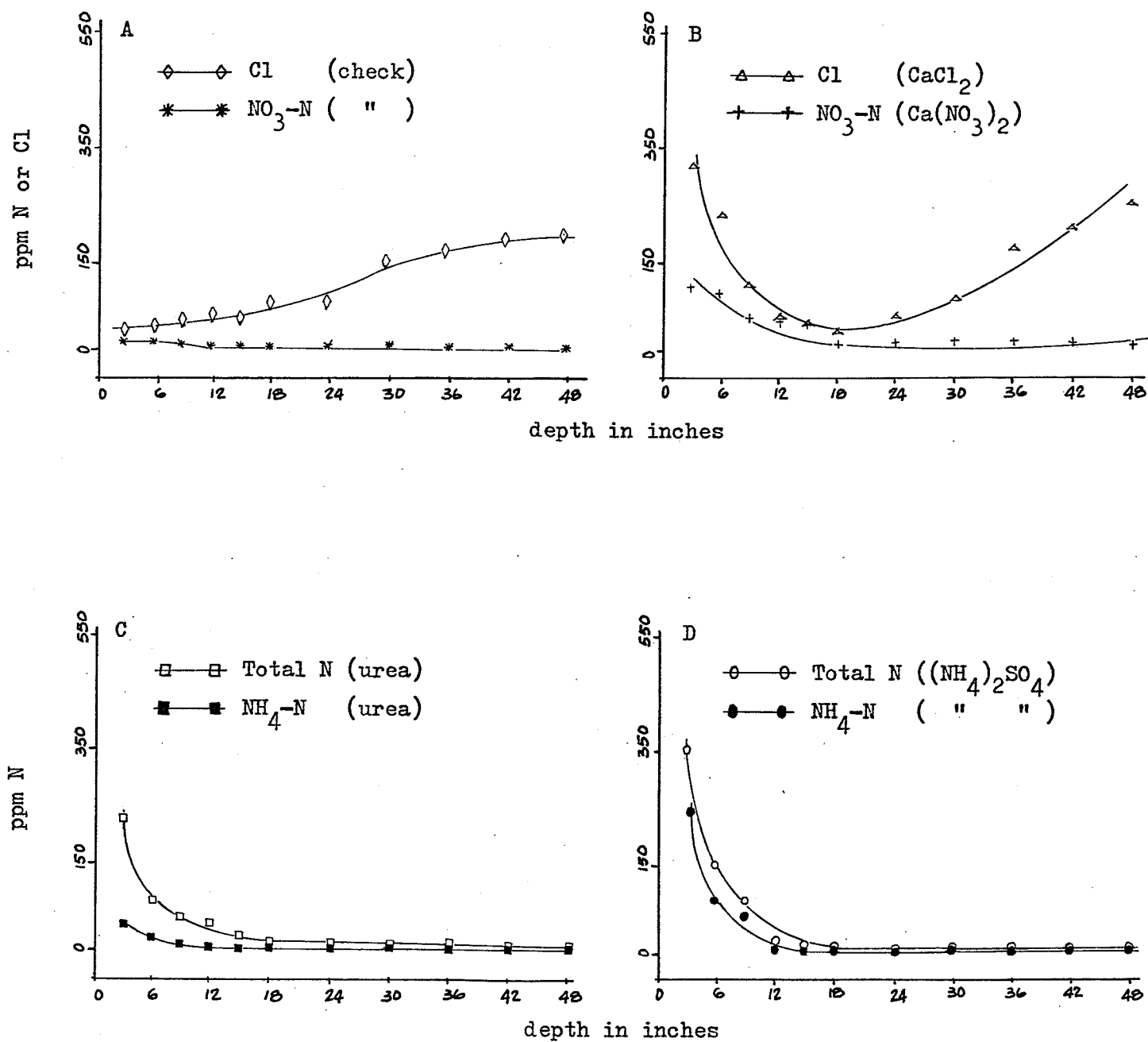
Fig. A9. Nitrogen and chloride distribution in the Red River
clay on August 11, 1971.
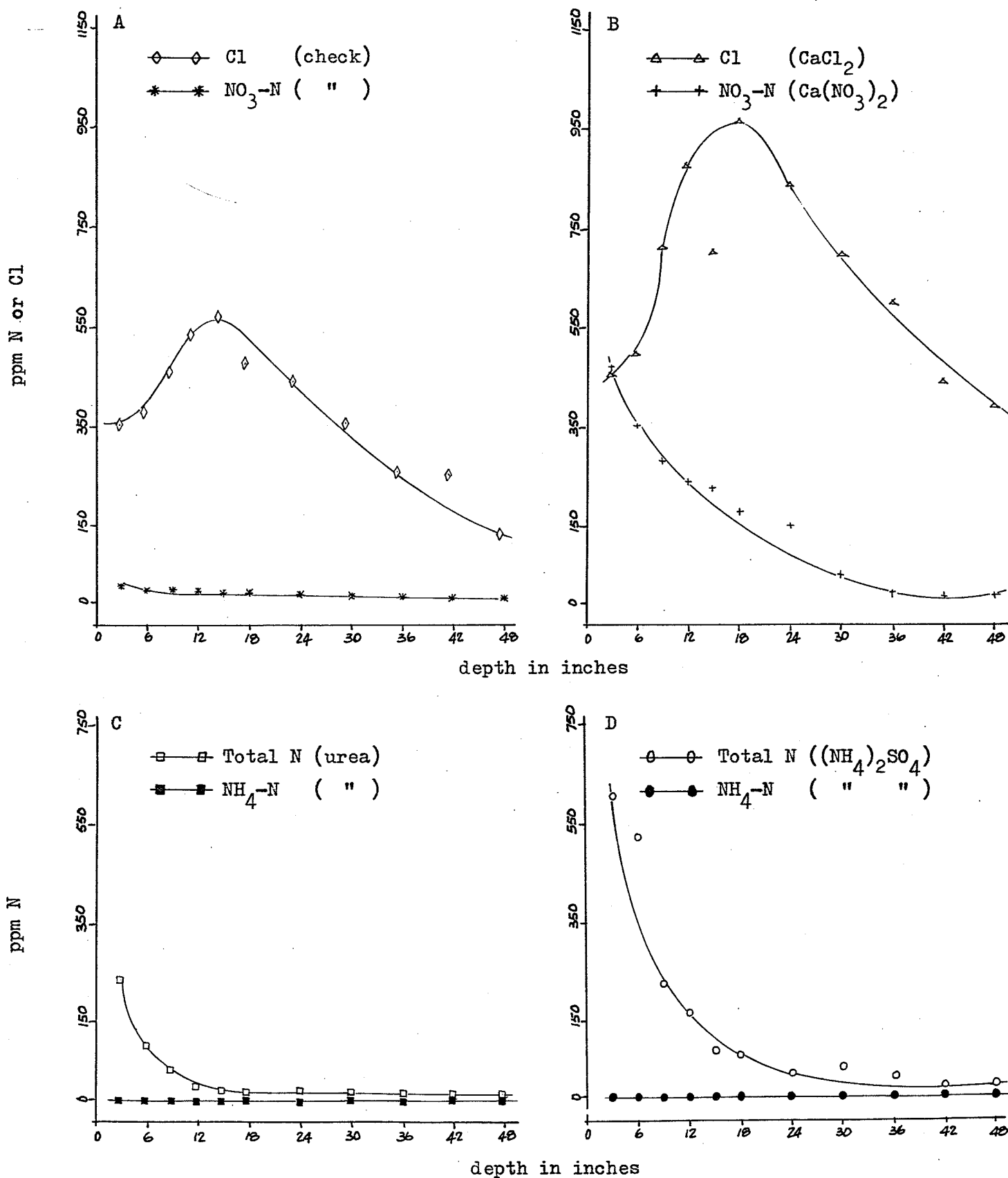
Fig. A10. Nitrogen and chloride distribution in the Portage loam
on August 13, 1971.
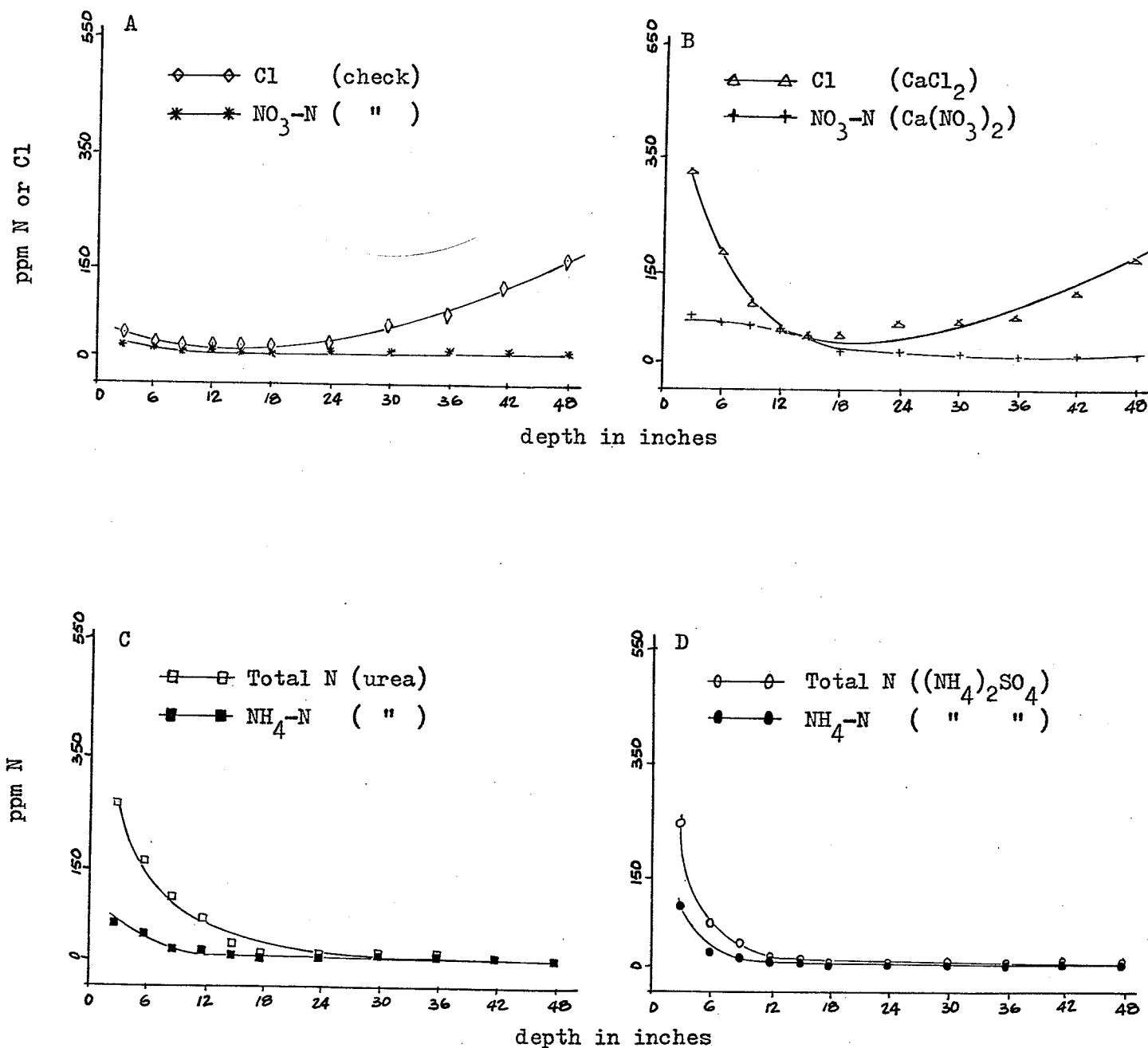
Fig. A11. Nitrogen and chloride distribution in the Red River
clay on August 25, 1971.

Fig. A12. Nitrogen and chloride distribution in the Portage loam on August 27, 1971.

Fig. A13. Nitrogen and chloride distribution in the Red River
clay on September 8, 1971.

Fig. A14. Nitrogen and chloride distribution in the Portage loam
on September 10, 1971.

Fig. A15. Nitrogen and chloride distribution in the Red River
clay on October 8, 1971.

Fig. A16. Nitrogen and chloride distribution in the Portage loam
on October 15, 1971.

Fig. A17. Nitrogen and chloride distribution in the Red River
clay on May 3, 1972.
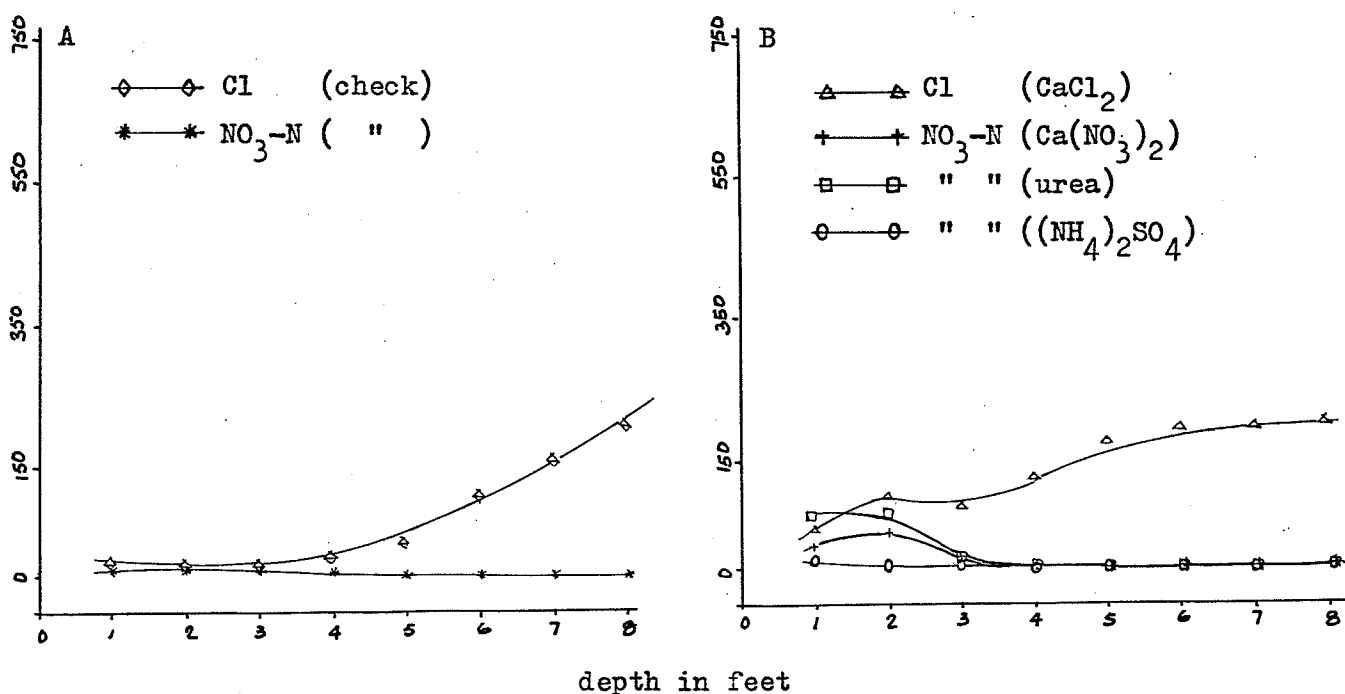
Fig. A18. Nitrogen and chloride distribution in the Red River
clay on October 17, 1972.
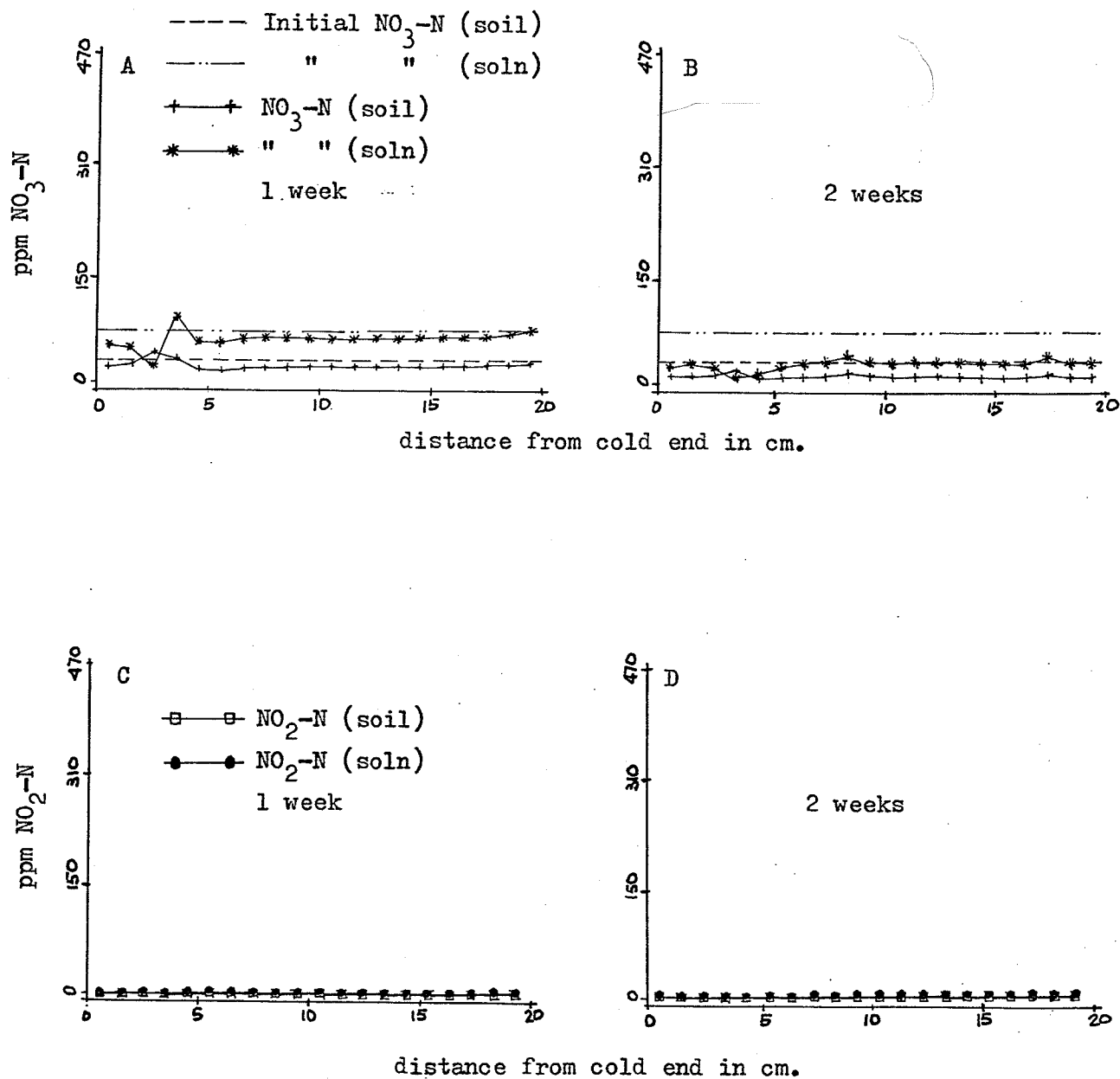
Fig. A19. Distribution of NO_3^- and NO_2^- in untreated Red River soil columns after being subjected to the thermal gradient (initial moisture content = 45%).
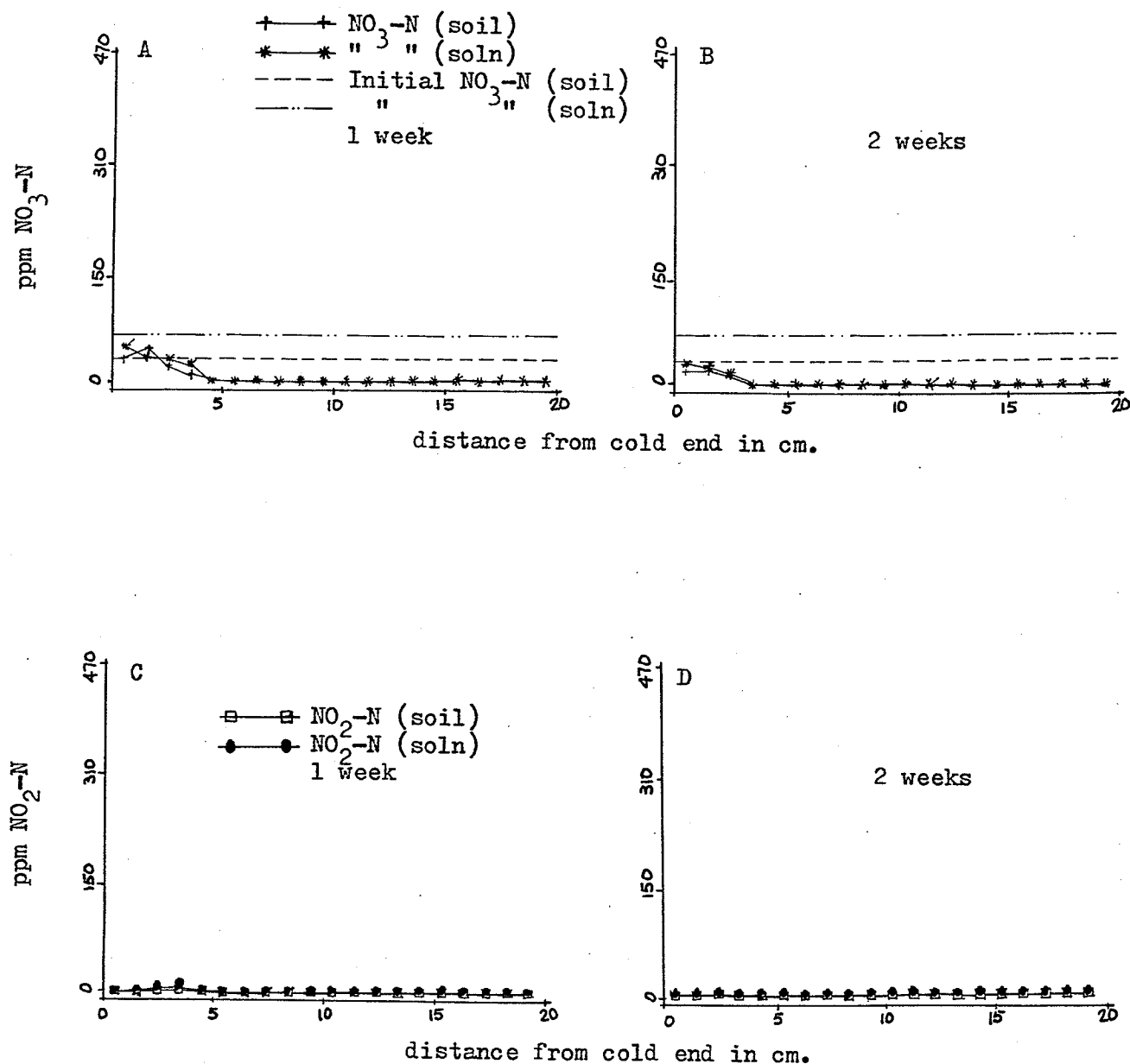
Fig. A20. Distribution of NO_3^- and NO_2^- in untreated Red River soil columns after being subjected to the thermal gradient (initial moisture content = 54%).
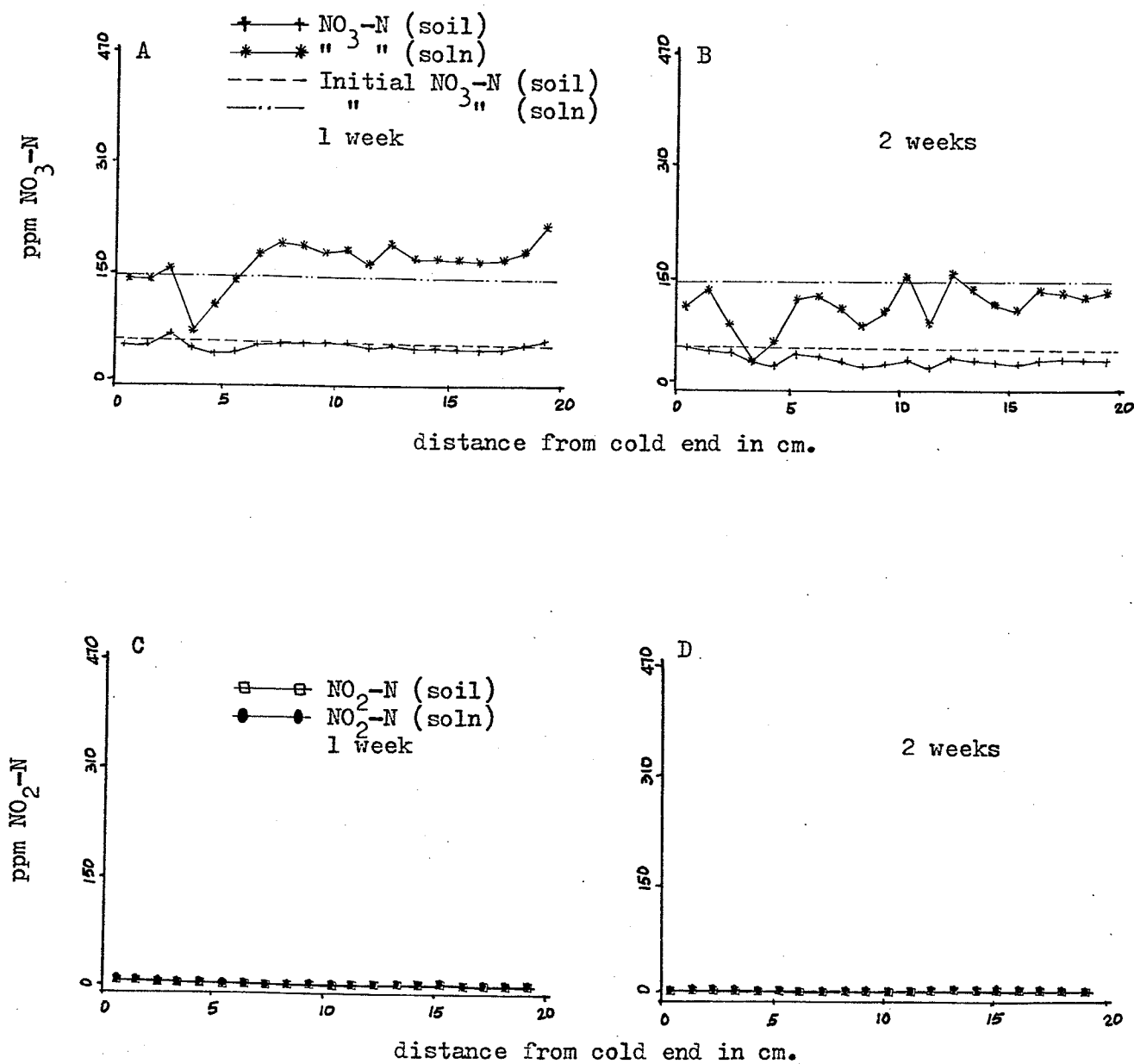
Fig. A21. Distribution of NO_3^- and NO_2^- in untreated Portage soil columns after being subjected to the thermal gradient (initial moisture content = 33%).
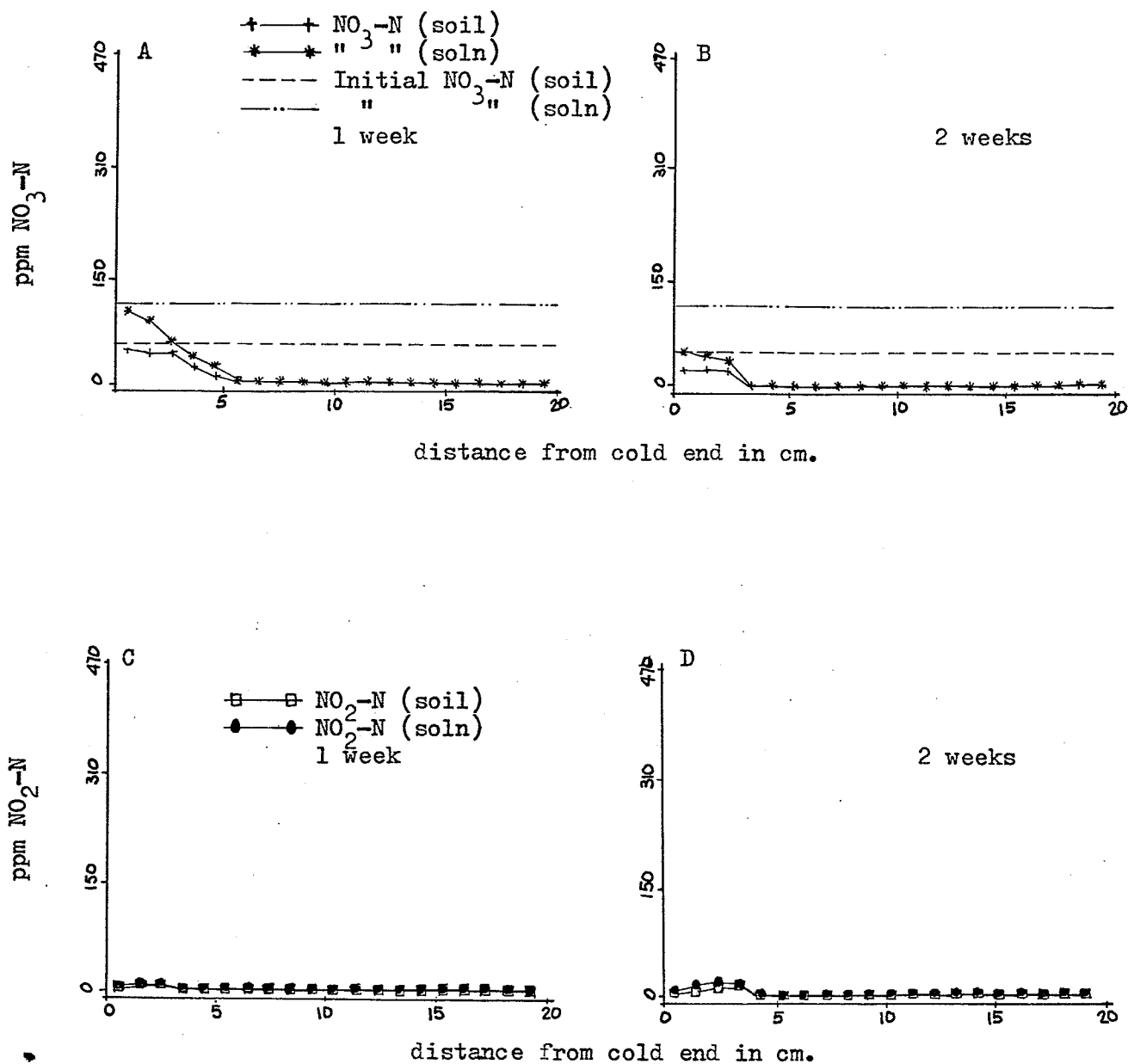
Fig. A22. Distribution of NO_3^- and NO_2^- in untreated Portage soil columns after being subjected to the thermal gradient (initial moisture content = 44%).