SOIL SOLUTION COMPOSITION OF MEDIUM BLACK & LATERITIC SOILS AS INFLUENCED BY ADDED ANHYDROUS AMMONIA & INCUBATION TIME

A Thesis Submitted
by

Mahipati Bhikaji Jadhav
B. Sc (Ag) First Class, M. P. K. V., Rahuri, 1974

to the

MAHATMA PHULE KRISHI VIDYAPEETH
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[illegible] TO [illegible]

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JADHAV SHRIPATI BALAJI
B.Sc.(Agri.), I Class, M.P.K.V. Rahuri, 1974

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1	Chairman and Research guide	N.K. Savant
2	Member	G.K. Zende
3	Member	P.[illegible] Kalbhor

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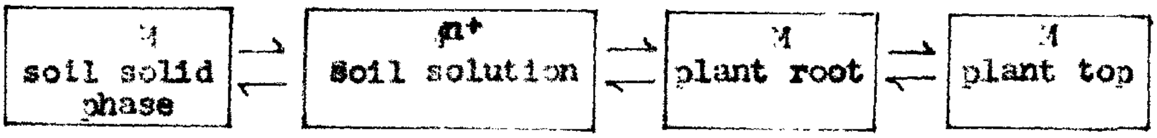
CONTENTS

Chapter 1

INTRODUCTION

The soil solution is a medium that bathes plant roots. Now there exists sufficient convincing evidence which supports the concept of soil solution as the expression of soil chemical environment that markedly influences ion-uptake by plants and eventually plant response. In other words, importance of soil solution in mineral nutrition of plants is well documented.

The overall picture of ion-uptake in the soil-plant system (Fried and Broeshart, 1967) can be summarized as :



The effective concentration (activity) of ions in solution which is often described as "intensity factor" of nutrient availability to plants, is governed by several chemical equilibria occurring in the soil system. The pH of soil solution is one of the master variables which markedly influences numerous soil chemical reactions, thereby regulating concentration of various ion species in soil solution. Ion exchange equilibria constitute another group of reactions which occur at soil solid-solution interface and are very closely associated with changes in soil-solution composition.

When anhydrous NH_3 is injected into soil, there is dramatic rise in soil pH and protonation of NH_3 results in formation of NH_4 ions in presence of soil water. Both these consequences in ammoniated-soil are likely to disturb existing soil chemical equilibria in soil system and in turn soil solution composition.

No data were available in literature on soil solution composition as influenced by addition of anhydrous NH_3. The objective of the present research project was therefore to collect data on soil solution composition of two tropical soils (medium black and lateritic soils), containing 1/3 atm percentage moisture as influenced by addition of anhydrous NH_3 and incubation time.

Chapter 2

REVIEW OF LITERATURE

The soil solution is a complex quasi-equilibrium aqueous solution of mainly electrolytes that occurs in three-phase soil system under unsaturated moisture regime (Pearson 1971). Similar definition of soil solution has been also given by Wiklander (1958). According to Glossary of Soil Science Terms (1975), it is an aqueous liquid phase of soil and its solutes. Realizing the importance of soil solution characteristics in fertilizer use technology, in 1970, Yamasaki and Kishita have reported an excellent historical review of studies on the soil solution composition and factors affecting it. Soil solution composition data (Table 1) compiled by Fried and Shapiro (1961) indicate that all the major nutrient ions except phosphate are normally present in it at concentration approximating 10^{-3} to 10^{-4} M. Phosphate-P concentration is usually low in the range of 10^{-5} to 10^{-6} M.

Reitemeiyer and Richards (1944) obtained soil solution of saline soil by pressure membrane method and noticed very high concentration being 1.67 N as to the sum of Ca, Mg, Na and K. Lower concentrations of soil solution for nonsaline soils were obtained by Burd and Martin (1924), the normality of Ca + Mg + Na + K varing between 0.008 to 0.017 N .

Table 1 : Soil Solution Composition *

Element	Range of all soils	Acid soil	Calcareous soil
		m mole/liter	
Ca	0.5-38	3.4	14
Mg	0.7-100	1.9	7
K	0.2-10	0.7	1
Na	0.4-150	1.0	29
N	0.16-55	12.1	13
P	0.001-1	0.007	0.03
S	0.1-150	0.5	24
Cl	0.2-230	1.1	20

* Compiled by Fried and Shapiro (1961).

2.1 : Chemical equilibria and soil solution :

The ion species in soil solution are drawn from and are in quasi-equilibrium with many constituents of soil solid phase, such as (i) free, soluble salts (ii) adsorbed salts (iii) sparingly soluble and/or precipitated compounds (iv) exchangeable ions and (v) ion-pairs. It is, therefore, obvious to expect existance of several simultaneous chemical equilibria in soil system.

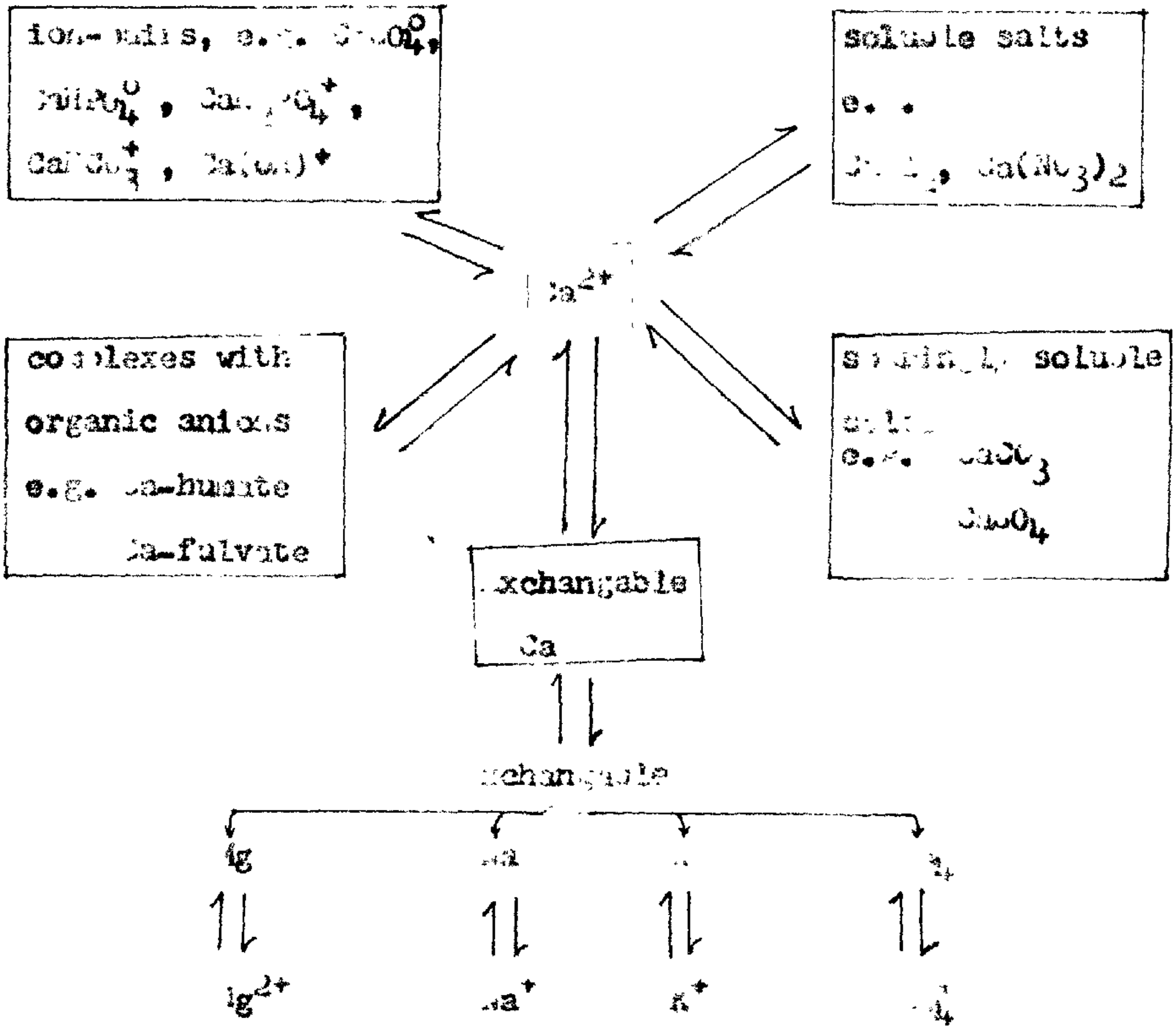


Fig 1: Calcium equilibria in soil solution of calcareous soil.

These calcium equilibria (Fig 1) may serve as an example of such simultaneous chemical equilibria in a natural soil solution. This scheme shows that thermodynamic concentration of Ca^{2+} in soil solution is in equilibrium simultaneously with

(i) ion pairs (ii) sparingly soluble salts (iii)exchangeable Ca. These equilibria, of course, are affected by activities of other electrolytes and ions in soil solution.

From the above example of simultaneous Ca equilibria, one can recognize that soil solution composition at a given moisture regime and at a given time is a resultant effect of variety of reactions or processes (Adams, 1974, Oster and McNeal 1971), such as :

a) acid-base reactions,

b) gas solution reactions,

c) precipitation and dissolution reactions,

d) formation of coordinate complex of metal ion and ligands,

e) oxidation-reduction processes,

f) exchange reactions at the solid-liquid interface,

g) anion exclusion (negative adsorption),

h) hydrolytic reactions.

Acid-base equilibria play a marked role in determining soil solution composition. Therefore, soil (solution) pH is one of the "master variable" which largely influences most of simultaneous chemical equilibria and eventually governs soil solution composition. While describing chemical equilibria of metal chelates in soil, Norvell (1972) has summarized the effects of soil pH on concentration and/or activity of Ca^{2+}, Mg^{2+}, Al^{3+} and Fe^{3+} in soil solution (Fig 2).

d) Solubility product expression of $CaCO_3$

$$\frac{(Ca^{2+})\ (CO_3^{2-})}{(CaCO_3)} = K_{CaCO_3} = 10^{-8.3}$$

Using the above chemical equilibria, the pH of $CaCO_3$-H_2O-CO_2 system can be defined as :

$$pH = K + \frac{1}{2}\,p^{Ca} + \frac{1}{2}\,p^{CO_2}$$

When the $p^{CO_2} = 10^{-3.5}$ atm and pH of $CaCO_3$-H_2O-CO_2 system works out to be 8.4 (Garrels and Christ, 1965). The pH (H_2O) values of calcareous soils when in equilibrium with atmosphere are also reported to be in vicinity of 8.4 (Turner, 1958). In other words, the pH (H_2O) of calcareous soil solution appears to be regulated by $CaCO_3$-H_2O-CO_2 system. The soil solution pH under submerged condition is mainly determined by $FeCO_3$-H_2O-CO_2 system and/or $MnCO_3$-H_2O-CO_2 system (Ponnamperuma, 1972).

Dissolution and precipitation reactions exert significant influence on chemical equilibria in soil solution. Solubility expressions of solid-soil constituents have helped in understanding variation in soil solution composition(Dutt,1962; Oster and McNeal 1971, Nakayama 1971). In general dissolution of an inorganic salt in aqueous system may be written as :

$$M_mA_n\ (s) \rightleftharpoons m\,M^{n+}\ (aq) + n\,A^{m+}\ (aq)$$

at equilibrium,

$$M_mA_n\ (s) = (a_{M^{n+}})^m\ (a_{A^{m-}})^n$$

solubility product (K_{sp}) expression is,

$$K_{sp}\,(M_mA_n) = (a\,M^{n+})^m\;(a\,A^{m-})^n$$

Whenever the activity of a nutrient ion in the soil solution exceeds the equilibrium concentration of a mineral or inorganic solid-phase, it begins to precipitate out. Conversely, whenever a nutrient ion activity in the soil solution drops below the equilibrium solubility of a solid phase (or salt), that phase begins to dissolve. It may therefore, be possible to characterise solubility of sulphastes, chlorides, fluorides and phosphates of Ca, Mg, Fe, Mn etc, in soil solution according to general solubility product principles. However, precautions are necessary in applying K_{sp} as there are some problems associated with determination and application of it. The ions produced as a result of dissolution process frequently undergo many chemical reactions, such as acid-base reactions, complex formations, ion-pair formations etc (Nakayama, 1971, Stumm and Morgan 1970). For example, the solubility of $FePO_4$ (s) will not only depend on (Fe^{3+}) (PO_4^{3-}) but also on acid-base equilibria (e.g. formation of $FeHPO_4^{+}$, $FeH_2PO_4^{+}$). The available compilation of K_{sp} data in literature has often shown variation.

In soil system, incongruent solubility is also prevalent, for example, added soluble phosphate salts dissolve incongruently with formation of relatively insoluble salts. Similarly $MgCO_3$ (s) i.e. magnesite, added to soil through liming material will dissolve incongruently with formation of $Mg(OH)_2$ (s).

The elements such as C, N, O, S, Fe and Mn are present in soil system which are often prone to redox changes. Redox equilibria can be best illustrated pH or Eh-pH diagrams (Garrels and Christ 1965, Sillen 1967, Stumm and Morgan 1970) which show, in a comprehensive way (a) how activity of protons and electrons simultaneously influence the chemical equilibria and (b) what solid phase controls concentration, (Ponnamperuma 1972).

Formation of aquocomplexes or hydroxocomplexes through co-ordination reactions between metal ions and water molecules is common in aqueous system analogous to soil solution. Such reaction has been described as hydrolysis or protolysis of metal ions. The formation of soluble aquocomplexes can be adequately described by hydrolysis equilibrium constant. However, some of these reactions are relatively slow and the kinetic intermediates are metastable or unstable. The following two rules may govern hydrolysis equilibria in soil solution (Stumm and Morgan 1970) . (a) In aqueous phase, the metal ions tend to protolyse more with decrease in activity of protons (increase in pH of aqueous system).(b) The fraction of polynuclear complexes in a solution decreases on dilution. For more detailed information on behaviour of metal ions in aqueous solution (such as soil solution) and their co-ordinative processes, reviews by Sillen (1967), Garrels and Christ (1965) Stumm and Morgan (1970) may be consulted.

As a result of cation exchange, the cations are distributed between exchanger phase (adsorbed phase) and soil solution (liquid) phase. Assuming the cation exchange reaction is reversible and stoichiometric chemical reaction (which obeys the law of mass action), it can be written as :

$$\nu_A A_{(ad)} + \nu_B B \underset{K_{(A \to B)}}{\overset{K_{(B \to A)}}{\rightleftharpoons}} \nu_A A + \nu B_{(ad)}$$

Where ν with substripts A and B represent number of reacting cations of A and B respectively, (ad) denotes cations in exchanger or adsorbed phase, while absence of suffix denotes ions in soil solution phase.

Various cation exchange equations have been used in soil science to describe quantitatively, the distribution of cations in two phases of soil system.

Using thermodynamic approach suggested by Argersinger, cation exchange equilibria can be written as (Gains and Thomas 1953):

$$\frac{a_{B(ad)}^{\nu_B}\, a_A^{\nu_A}}{a_{A(ad)}^{\nu_A}\, a_B^{\nu_B}} = e^{-\Delta G^0/RT}$$

Where R = universal gas constant
T = absolute temperature
G^o = standard free energy change
= activity
K = thermodynamic equilibrium constant
e = base of natural log.

The equation can be written by substituting activity of adsorbed ions as ;

$$\frac{f_B^{\nu_B}\ \underline{N}_B^{\nu_B}\ a_A^{\nu_A}}{f_A^{\nu_A}\ \underline{N}_A^{A}\ a_B^{\nu_B}} = K_{(B \rightarrow A)}$$

Where f = activity coefficient

$\underline{N}$ = Mole fraction of adsorbed cation.

The values of thermodynamic equilibrium constants have been calculated by applying the above Argersingers thermodynamic approach to the exchange isotherms for various systems, such as K-Ka, K-Ca, K-Mg, Mg-Ca (Jensen and Babcock, 1963, Jensen Van Bladel and Menzel, 1969). It can therefore, be concluded that the theory appears to be valid for the symmetrical as well as unsymmetrical cation exchange equilibria at soil solid-solution interface.

2.2 Ionic activity-concentration relationship in soil solution:

In order to make the discussion on various chemical equilibria in soil solution thermodynamically meaningful and to be able to predict crop response from the soil solution composition data, it seems highly desirable to correct the measured ionic concentrations of soil solution to their activities . In this connection ionic strength and activity coefficient, concepts of physical chemistry are important.

The ionic strength (μ) of an electrolyte solution is a measure of intensity of the electrical field in the solution and is mathematically defined as :

$$\mu = \tfrac{1}{2} \sum C_i \ z_i^2$$

Where C_i = measured concentration of ion(i)/ mole/liter

Z_i = valence of ion (i)

According to Debye-Huckel theory the individual ion activity coefficient (f_i) in dilute aqueous solution can be defined as :

$$-\log f_i = \frac{A z_i^2 (\mu)^{\frac{1}{2}}}{1 + B a_i (\mu)^{\frac{1}{2}}}$$

where A & B are constants characteristic of the solvent (in this case water) at a specified temperature and pressure. μ is ionic strength and a_i ion size parameter of each ion in aqueous solution.

The activity (in simple terms effective concentration) of an individual ions (i) is

$$a_i = f_i C_i$$

Further, the other thermodynamic reaction constants required for correcting the actual concentration of soil-solution ions to their activities are (i) ion-pair dissociation constant, (ii) weak acid-weak base dissociation constant, (iii) hydrolysis constants of metal ions and (iv) solubility constants of certain gases(Adams 1971).

In absence of ion-pairs, measured ionic concentration is equal to actual concentration and calculations of activity of ions are calculated according to the above equations. In the case of mixed electrolyte (similar to that of soil solution), the measured ion concentration is always more than the actual ion concentration. This problem is solved by the method of successive approximations till there is no further change in two successive values. A mathematical procedure alongwith suitable examples for calculating actual ionic strength and subsequently ionic activity in pure, as well as in mixed dilute electrolyte aqueous solutions analogous to soil solution is given by Adams (1971).

2.3 Effect of added anhydrous NH_3 on soil solution :

When anhydrous NH_3 is applied to soil using injection technique, it interacts with soil-solid phase, organic as well as inorganic, and is retained in soil through physical and/or chemical mechanisms. Mortland (1966), Parr and Papendick, (1966) and recently Shimpi (1973) have given excellent reviews of anhydrous NH_3-soil colloid interactions. A summary of physical, chemical, and biochemical fate of anhydrous NH_3 injected into soil is presented in Fig 3.

The pH and ionic composition of soil within zone of injection of anhydrous NH_3 are totally unlike the surrounding soil. Fertilizers containing NH_4^+ are known to influence soil pH

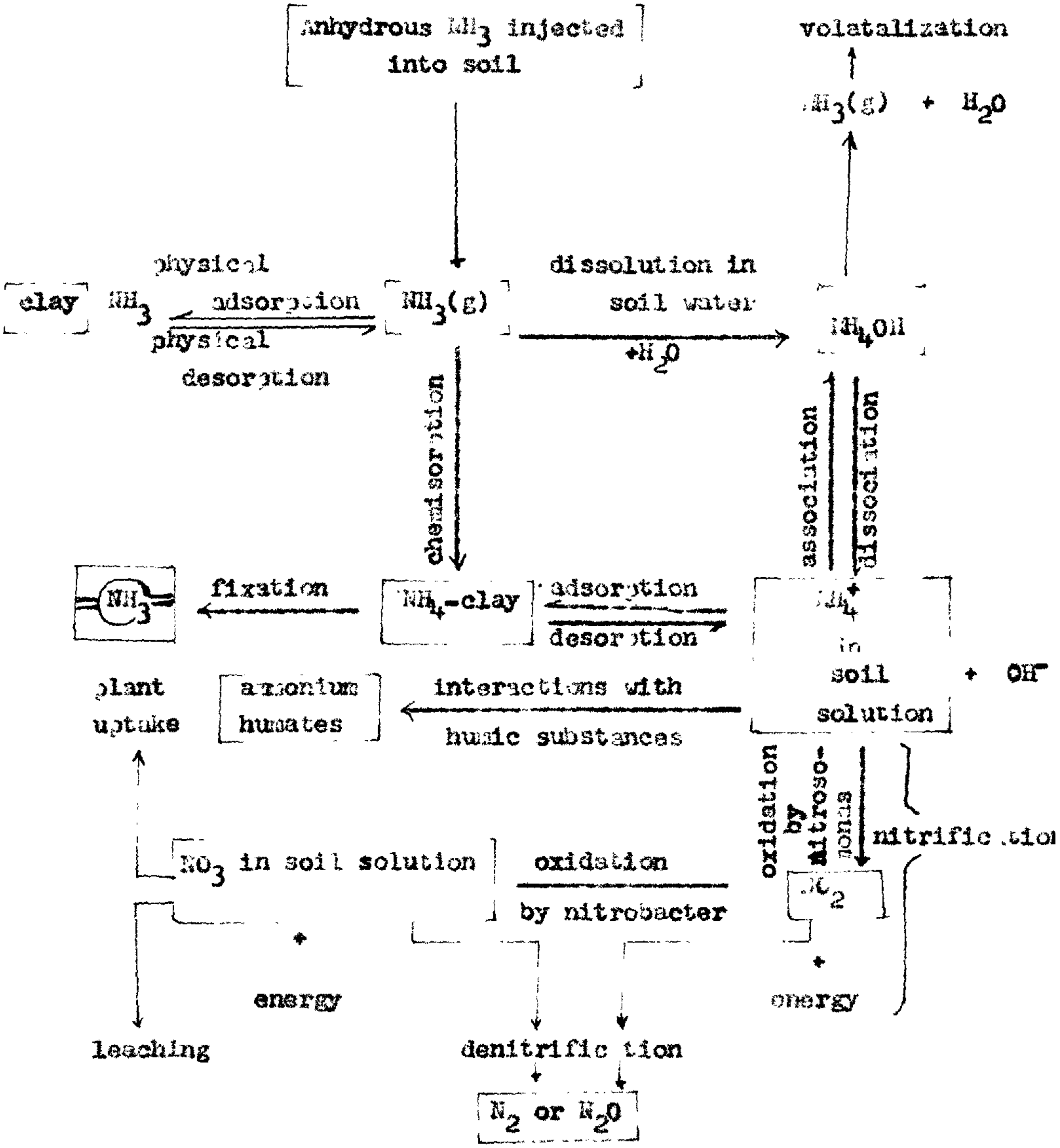


Fig 3 : Fate of anhydrous ammonia injected into soil- physical, chemical and biological reactions.

or soil-solution pH (Isensee and Walsh, 1971; Passioura and Wetselaar, 1972). Khengre (1975) noticed pH 9.7 near anhydrous NH_3-injection point in a vertisol. However, as nitrification occurred with incubation time he reported decrease in soil pH upto 6.6. After anhydrous ammonia injection, it can exist in soil in two forms, ionized and nonionized as :

$$NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

The relative proportion of these two forms are determined by pH of soil solution. The respective percentages of free ammonia existing at pH 6.0 compared to that at pH 9.0 would be of the order of 0.1 per cent and 50 per cent respectively (Parr and Papendick, 1965).

As a result of dramatic changes in soil pH and eventually in soil-solution pH, due to anhydrous NH_3 injection into soil, dissolution-precipitation reactions are the first chemical reactions likely to be influenced. When anhydrous NH_3 was applied to soils, increase in phosphates in soil solution was observed by Peach, as reported by Mortland (1965). The solubility of mineral forms of P in soils appears to be affected by the change in pH on application of NH_3. It is likely in the course of these interactions that some of the ammonium phosphate compounds might be formed (Mortland, 1966).

Iglovikov and Kulakov (1970) observed increase in mobile forms of P, K and Ca in the derno-podzolic soil when it was treated with anhydrous NH_3. McDowell and Smith (1958) noticed 5 to 6 times increase in n in saturation extract of ammonia-treated soil as compared with that of check soil.

The changes in soil pH on application of anhydrous NH_3, not only affect solubility of inorganic soil constituents, but also solubility of soil organic matter. Laboratory lysimetric trials conducted by Nemec (1971) revealed maximum solubilization of soil humic substances by anhydrous NH_3 application as compared with other N-carriers application. By and large, similar observations were reported by McDowell and Smith (1958), Mangum and Young (1965).

There is a marked increase in concentration of NH_4^+ as a result of protonation and/or dissolution reactions in soil water surrounding the injection point or band. The NH_4^+ ions thus formed, may also enter the exchange reactions as :

$$\boxed{\text{clay}}M + nNH_4^+ \rightleftharpoons M^{n+} + nNH_4\boxed{\text{clay}}$$

and concentration of displaced cations may increase in soil solution. Displacement of exchangeable K by heavy application of fertilizers containing NH_4^+ has been observed by Abruna **et al.**, (1958). Iglovikov and Kulakov (1970), also noticed higher contents of mobile Ca, Mg and Na near the point of application of anhydrous NH_3.

According to Mortland, (1966), NH_3 may be retained by Ca-$\boxed{\text{Clay}}$ as :

$$Ca\ (H_2O)\ x\ \boxed{\text{clay}} + 2NH_3 \longrightarrow Ca\ (OH)_2 + 2NH_4\ \boxed{\text{clay}} + (x-2)H_2O$$

Such retention reaction may be operative in calcareous soils which would result in increase in Ca^{2+} in solution. However, it appears that these Ca^{2+} and Mg^{2+} are effectively removed from soil solution by precipitation as respective or mixed carbonates, thereby preventing any extensive re-exchange of NH_4 from sites previously occupied by these cations (DuPlesis, 1962).

It is apparent from the above review of literature, that very limited data are available on direct effect of applied NH_3 on soil solution composition of even temperate soils. In so far as tropical soils are concerned, such data, hitherto, are not available at all. For efficient use of anhydrous ammonia as a source of N to plants, under tropical conditions, data on soil solution composition of ammoniated soil are necessary.

Chapter 3

MATERIALS, METHODS AND [illegible]

3.1 Materials :

3.1.1 Soils :

Medium black soil (vertisol, 0-20 cm, < 2 mm) from Central Campus Farm, MPKV, Rahuri (Block [illegible]) and lateritic soil (0-20 cm, < 2 mm) from Agricultural Research Station, Radhanagari (Dist. Kolhapur) were used in the investigation. Some of the physical and chemical properties of the soils are given in Tables 2 and 3 respectively.

Table 2 : Physical properties of the medium black and lateritic soils used

Property	Medium black soil	Lateritic soil
~~Sand %~~ clay%	54.10	36.60
Silt %	29.00	34.10
~~Clay %~~ sand%	15.90	29.30
Textural class	Clay	Clay loam
0 atm percentage	70.50	55.00
1/3 atm percentage	31.60	26.86
3 atm percentage	27.10	23.00
15 atm percentage	24.93	21.12

Table 3 : Chemical properties of the medium black and lateritic soils used

Property	Medium black soil	Lateritic soil
pH (H_2O) 1:1	8.1	5.9
EC m mho/cm	1.12	0.27
Total nitrogen (%)	0.07	0.10
NH_4^+ - N (mg/100 g)	2.25	3.45
NO_3^- - N (mg/100 g)	7.62	1.4
Organic carbon (%)	0.39	0.90
C:N ratio	5.6	9.00
$CaCO_3$ (%)	0.82	00.00
CEC (me/100 g)	41.40	15.90
Exchangeable Ca "	28.79	7.96
Exchangeable Mg "	5.82	3.67
Exchangeable Na "	3.39	1.60
Exchangeable K "	0.15	0.17
Available P (%)	0.0008	0.0023
Ammonia retention capacity (ARC) (mg/100 g)	161.53	1[illegible].72

3.1.2 Anhydrous ammonia :

Anhydrous ammonia gas cylinder (40 kg) was supplied by M/s Hica Chemicals Ltd. Pune, 411 005.

3.2 Methods :

3.2.1 Soil analysis :

These soils were analysed by adopting standard methods of analysis as shown in Table 4.

Table 4 : Methods used for soil analysis

Soil property	Method adopted	Reference
Particle size distribution	Bouyoucos Hydrometer	Bouyoucos(1962) Day (1965)
Moisture percentage	Tension plate pressure plate or pressure membrane	Richards (1965) Black (1965) Day *et al.*, (1967)
Ammonia retention capacity (ARC)	Pepandick and Parr as modified by Shimpi (1973)	Pepandick and Parr (1965)
Inorganic forms of nitrogen	Semimicro distillation	Bremner (1965)
Organic carbon	Walkley -Black	Allison (1965)
$CaCO_3$ equivalent(%)	Pressure calcimeter	Skinner *et al.*, (1958)
pH (H_2O) (1:1)	Potentiometric	Jackson (1958)
Electrical conductivity	Conductometric	Jackson (1958)
CEC and exchangeable cations	Rapid semimicro NH_4-OAc	Chapman (1965), Jackson (1958), Black (1965)
Available 'P'	Bray-1 and Olsen	Bray and Kurtz (1945) Olsen *et al.*, (1954)

3.3 Experimental :

3.3.1 Ammoniation technique:

Fabrication and calibration of anhydrous NH_3 injector apparatus used in the present investigation was similar to that of Pepandick and Parr (1965). The methodology of determination of ammonia retention capacity (ARC) was that of Shimpi (1973), Sufficient quantities of soil were brought to 1/3 atm percentage moisture content and equilibrated for 20-24 hr at ambient room temperature. The premoistened soil samples were then ammoniated equal to 0 (check), 33, 66 and 100 per cent of its ARC .

3.3.2 Incubation technique :

Four lots of 650 g soil samples (in duplicate)containing 1/3 atm percentage moisture were ammoniated. These ammoniated soil samples were kept in suitable plastic bags, and their mouths were tied with strings to prevent loss of moisture during incubation. For proper aeration about 20 pin-holes were made in each plastic bag. The plastic bags were stored at 27 ± 3 C temperature and about 75 to 90 % humidity, in dark chamber.

3.3.3 Extraction of soil solution :

After 3, 35, 70 and 120-day incubation, soil solution was extracted using Richards' pressure membrane apparatus supplied by M/s Soil Moisture Equipment Co. California U.S.A. (Richards 1965; Black 1965). For the extraction of soil solution 15 atm air-pressure was applied for a period of 6 hr and 15 hr for medium black and lateritic soils respectively. Thirty ml of soil solution was collected after discarding 5-[illegible] ml of solution.

3.3.4 Soil solution analyses :

Immediately after collection of soil solution, it was analysed for pH, EC and organic carbon, NO_3^--N and NH_4^+- N content. After these analyses the soil solutions were stored at 4 C after addition of 2-3 drops of toluene, until all remaining chemical analyses were completed by adopting the procedures given in Table 5.

Table 5: Methods used for analyses of soil solution

Soil solution determination	Method adopted	Reference
pH (H_2O)	Potentiometric	Jackson (1958) Black (1965)
Electrical conductivity	Conductometric	Jackson (1958)
Organic carbon	Modified Walkey-Black	Jackson (1958) Black (1965)
Calcium and Magnesium	EDTA-titration	Jackson (1958)
Phosphate	Colorimetric using ascorbic acid as reductant	Watanabe and Olsen (1965)
Sulphate	Turbidimetry	Jackson (1958)
Chloride	Argentometry	Chapman and Pratt (1961)
Carbonate and Bicarbonate	Potentiometric	Parks *et al.*, (1971)
Iron	Colorimetric using O-phenanthroline	Parks *et al.*, (1971)
Manganese	Colorimetric, using potassium periodate	Black (1965)

3.3.5 Soil analysis :

Soil remaining after extraction of soil solution was analysed for NH_4OAc-extractable Ca and Mg (Table 4).

3.4 Calculations of undissociated NH_3 concentration and ionic activity, ionic concentration and activity of ions in soil solution:

a) Calculations of undissociated NH_3 concentration : (Bezdicek *et al.*, 1971)

Calculations of NH undissociated NH_3 concentration in soil solution were made on volume basis of water. The following calculations were used where the equilibrium constant for NH_4OH formation from NH_3 and H_2O equals :

$$K = (NH_4^+)(OH)/NH_3 = 1.8 \times 10^{-5}$$

combined with the autodissociation of water

$$(OH)(H^+) = 10^{-14})$$

$$K^1 = (NH_4^+)/(H^+)(NH_3) = 1.8 \times 10^{9}$$

total analytical ammonia was defined as

$$^{F}NH_3 = (NH_4^+) + (NH_3)$$

by combining the above two equations

$$K = \frac{^{F}NH_3 - (NH_3)}{(H^+)(NH_3)}$$

solving for NH_3

$$NH_3 = \frac{^{F}NH_3}{1.8 \times 10^{9}(H^+) + 1}$$

NH_3 for each sample was converted to moles/liter and calculation for NH_3 (mole/liter) were made .

b) Calculations of ionic activity, ionic concentration and activity of ions in soil solution (Adams 1971).

The measured concentrations of cations namely Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} and NH_4^{+} and anions namely CO_3^{2-}, HCO_3^{-}, Cl^{-}, SO_4^{2-} and NO_3^{-} in displaced soil solution were considered for the purpose of calculations.

i) Ionic strength (μ)

Ionic strength of soil solution was calculated by using following formula :

$$\mu = \tfrac{1}{2}\sum C_i z_i^2$$

Where μ = ionic strength

C_i = measured concentration of ion

Z_i = valancy of respective ion

= Total

ii) Ionic activity coefficient

Ionic activity cofficient of each ion was calculated according to the equation :

$$-\log f_i = \frac{A z_i^2 (\mu)^{1/2}}{1 + B a_i (\mu)^{1/2}}$$

Where f_i = activity coefficient of ion (i)

A and B are temperature dependent constants (A = 0.509 and B = 0.321 at 25 C).

means individual ion size parameter in angstrom units for the Debye-Huckel equation for activity coefficient. for Ca^{2+}, Mg^{2+}, NH_4^{+}, HCO_3^{-} and SO_4^{2-} are 6, [illegible], 2.5, 4.5 and 4 respectively.

iii) Ionic activity

Ionic activity of individual ion was calculated by using following equation.

$$\log a_i = \log f_i + \log C_i$$

Where a_i = activity of ion (i)

f_i = activity coefficient for ion (i)

C_i = measured concentration of ion (i)

iv) Ion-pair concentrations were calculated for $CaSO_4^{o}$, $MgSO_4^{o}$, $NH_4SO_4^{-}$, $CaHCO_3^{+}$ and $MgHCO_3^{+}$ using equations :

$$(CaSO_4^{o}) = \frac{(Ca^{2+})\ (SO_4^{2-})}{5.25 \times 10^{-3}}$$

$$MgSO_4^{o} = \frac{(Mg^{2+})\ (SO_4^{2-})}{5.58 \times 10^{-3}}$$

$$NH_4SO_4^{-} = \frac{(NH_4^{+})\ (SO_4^{2-})}{7.93 \times 10^{-2}}$$

$$CaHCO_3^{+} = \frac{(Ca^{2+})\ (HCO_3^{-})}{5.5 \times 10^{-2}}$$

$$MgHCO_3^{+} = \frac{(Mg^{2+})\ (HCO_3^{-})}{6.9 \times 10^{-2}}$$

v) Calculated ionic concentrations can be given as :

$$\left[\begin{array}{l}\text{Calculated ionic}\\ \text{concentration}\\ \text{moles/liter}\end{array}\right] = \left[\begin{array}{l}\text{Measured ion}\\ \text{concentration}\\ \text{moles/liter}\end{array}\right] - \left[\begin{array}{l}\text{ion-pairs}\\ \text{calculated}\\ \text{moles/liter}\end{array}\right]$$

Chapter 4

RESULTS AND DISCUSSION

Knowledge of soil solution characteristics is a valuable tool in making predictions of plant response to the soil chemical environment. Literature reviews published by Parr and Pepandick (1966), Mortland (1966), Shimasi (1973), and others, suggest that application of anhydrous NH_3 in soil would bring about dramatic changes in soil solution composition, probably through changes in chemical soil equilibria occurring in the NH_3-retention zone. It was, therefore, thought that probable changes in soil solution composition would alter soil chemical environment and eventually determine efficacy of anhydrous NH_3 as a source of N to plants. Hence attempt was made to study the soil solution composition of medium black and lateritic soils from Rahuri and Radhanagari respectively as influenced by anhydrous NH_3 application with time under laboratory conditions.

The soils were ammoniated at 4 levels namely 0, 33, 66, and 100 [illegible] so as to simulate concentration gradient of NH_4 and/or NH_3 that normally develops in a ammonia retention zone in soil. The soil solutions were extracted from the ammoniated-soil samples after incubation for varying periods (3, 35, 75 and 120 days) and maintained at 1/3 bar percentage (approx. Field capacity) by adopting Richards' pressure membrane method (Richards, 1941). According to Adams (1976, personal communications), the pressure-plate method alters some aspects of the true soil solution composition, namely,

i it effectively removes phosphates from soil solution,
ii it may add contaminants to the soil solution,
iii excess water may be needed to establish contiguous water film from membrane to soil particles (a dilution effect that cannot be corrected) and,
iv the high air pressure will alter CO_2 solubility and hence soil solution pH.

Keeping these limitations of the method of obtaining soil solution in view the changes in soil solution composition as influenced by anhydrous NH_3 application in the soils studied, reported in Tables 6 through 22 are discussed.

4.1 Soil solution pH

The changes in soil-solution pH as influenced by different levels of ammoniation and incubation time are shown in Fig. 4 and 5 .

Soil-solution pH of the check soils practically remained unchanged during the incubation period. After 3-day incubation, soil-solution pH values increased with increase in levels of ammoniation. The increases in soil solution pH values were 1.45 and 1.10 units for medium black and lateritic soils respectively, when these soils were ammoniated equal to 100 % AAC. Khengre (1975) ammoniated the medium black vertisol and noticed rise in soil pH values by about 2.0 units . Soil-solution pH appears to be determined by the following dissociation reaction (Adams, 1971).

$$1.8 \times 10^{-5} = \frac{(NH_4^+)\ (OH^-)}{(NH_3\ (\ aq)\ )}$$

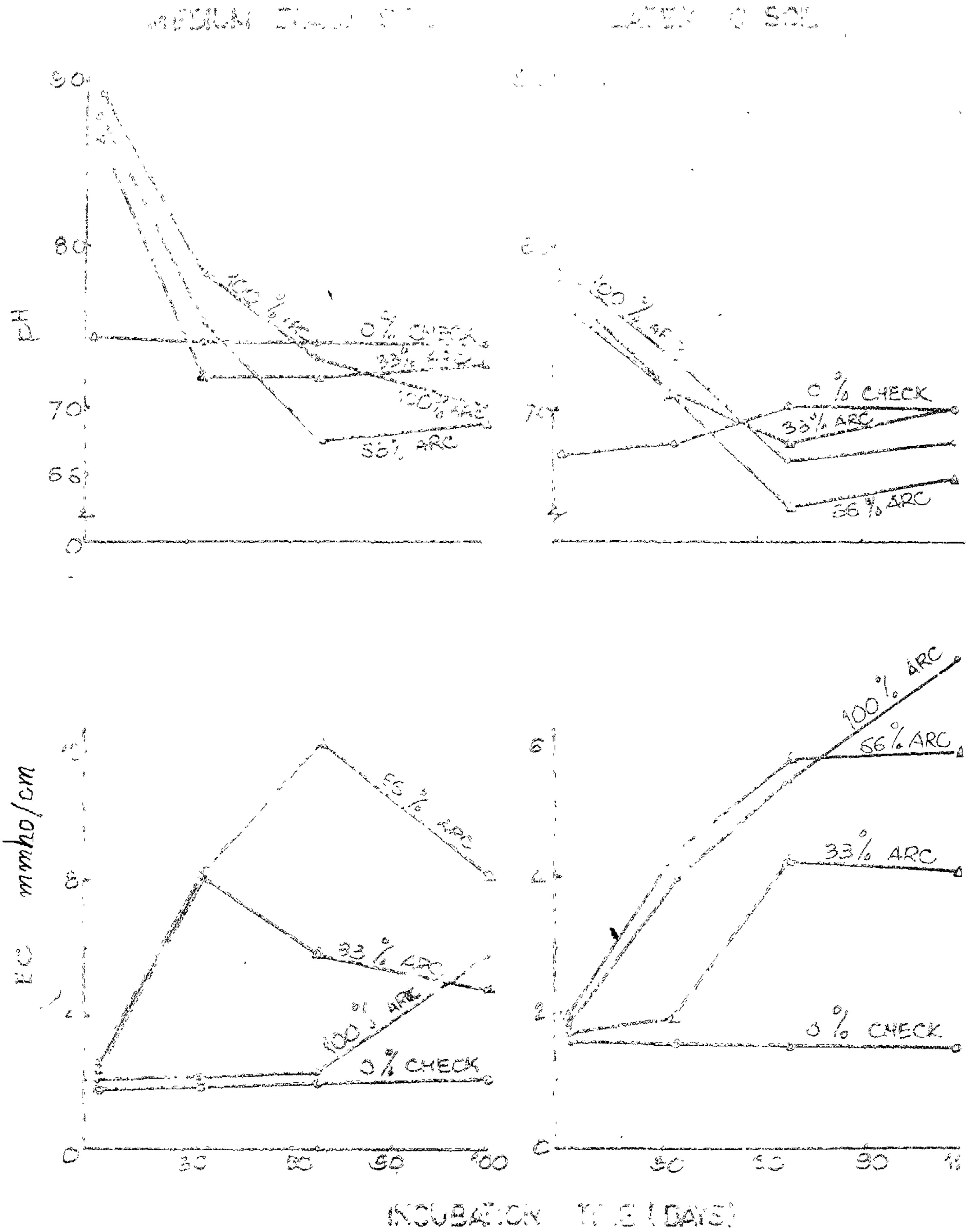
Soil-solution pH of the ammoniated soils decreased after 35-day incubation, mainly due to acidifying effect of nitrification process. Data given in Tables17 and 18 shows production of NO_3^- as a result of oxidation of NH_4^+ and concomitant disappearance of NH_4^+ from soil solution. The lowest pH was observed when the soils were ammoniated equal to 66 % AAC and incubated for 70 days.

4.2 Soil-solution EC:

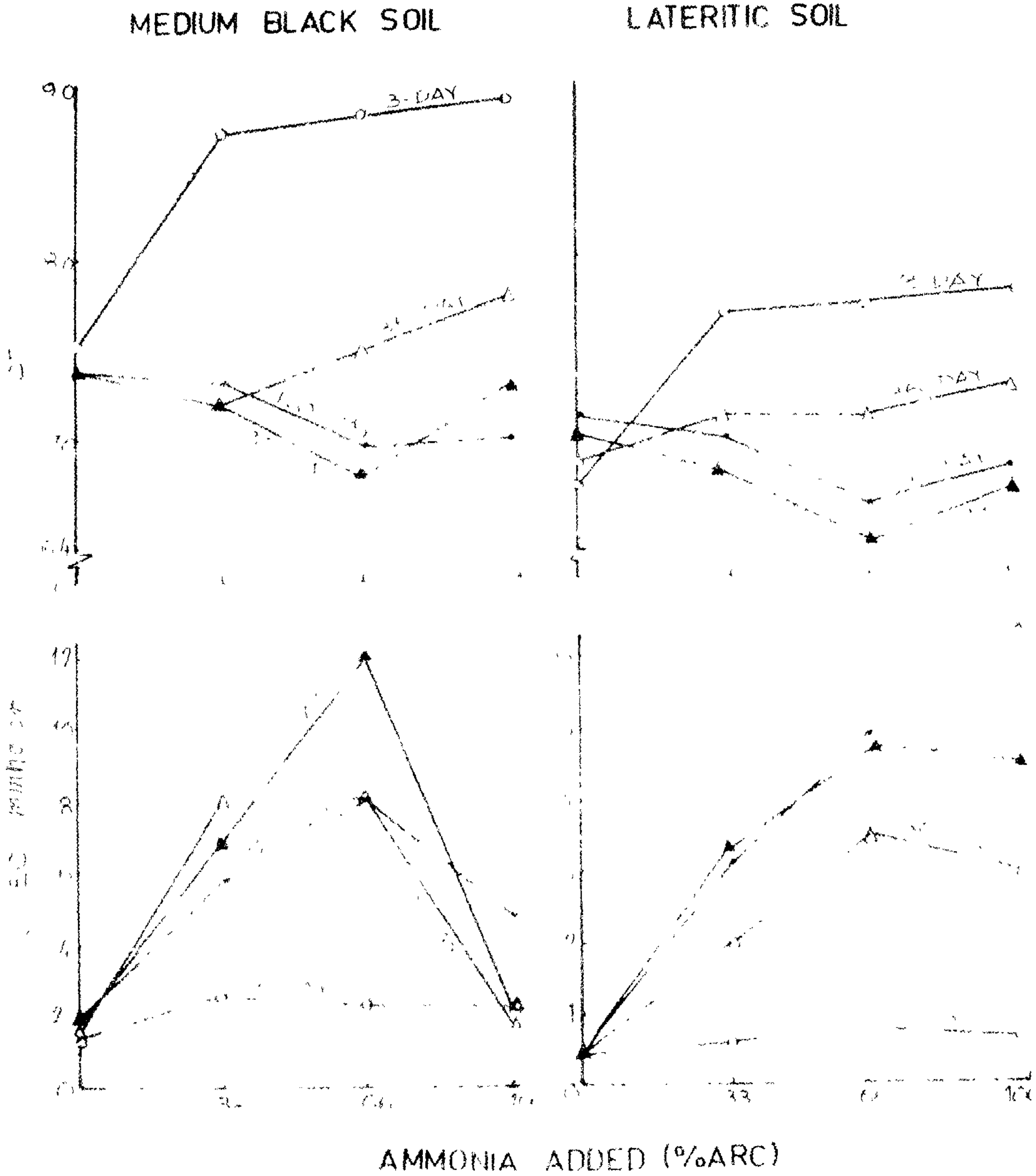
The changes in soil-solution EC as influenced by different levels of ammoniation and incubation time are shown in Table 6 and Fig 4 and 5.

Table 6 : Soil-solution pH and EC of the soil studied as influenced by added anhydrous NH_3 and incubation time

NH_3 added (% AMC)	Incubation time (days)	Medium black soil		Lateritic soil	
		pH	EC (m mho/cm)	pH	EC (m mho/cm)
0 (check)	3	7.45	1.80	6.70	0.47
	35	7.40	1.80	6.60	0.48
	70	7.40	1.90	7.00	0.50
	120	7.40	1.95	7.00	0.50
33	3	8.70	2.53	7.60	0.58
	35	7.20	8.01	7.10	2.00
	70	7.20	6.80	6.80	3.30
	120	7.30	5.80	7.00	3.20
66	3	8.80	2.34	7.70	0.82
	35	7.50	8.00	7.10	3.42
	70	6.80	12.00	6.40	4.70
	120	6.90	8.00	6.60	4.80
100	3	8.90	2.23	7.80	0.69
	35	7.80	1.90	7.30	3.08
	70	7.30	2.20	6.70	4.50
	120	7.00	4.80	6.80	6.36


pH
90
80
70
66
0
100 % ARC
0 % CHECK
33% ARC
100% ARC
33% ARC
100 % ARC
0 % CHECK
33% ARC
66 % ARC
EC mmho/cm
6
4
2
0
66 % ARC
33 % ARC
100 % ARC
0 % CHECK
100 % ARC
66 % ARC
33 % ARC
0 % CHECK
30
60
90
100
INCUBATION TIME (DAYS)

4 : [illegible] the [illegible]


MEDIUM BLACK SOIL
LATERITIC SOIL
3-DAY
9.0
8.0
3-DAY
16-DAY
EC mmhos
12
8
4
2
0
33
100
AMMONIA ADDED (%ARC)

5 [illegible] in [illegible] of th[illegible]

[illegible]

[illegible].

Electrical conductivity of an electrolyte aqueous solution can be given by the following equation :

$E = KC$

Where, E = electrical conductivity of an electrolyte solution at 25 C,

K K = cell constant at 25 C,

C = electrical conductance .

After 3-day incubation soil-solution EC values were virtuall unchanged, at all levels of ammoniation of the soils, which may be due to incomplete exchange reactions, and practically absence of nitrification (Table 9 and 17, 18 respectively). In general, soil-solution EC of the ammoniated soils increased with incubation time except that of medium black soil ammoniated equal to 100 % AHC upto 70 day incubation. These results are supported by increase in measured concentration of cations in soil solution of the ammoniated soils with time. As incubation progresses, added NH_3 to soil is nitrified to nitrates (McIntosh and Fredrick, 1958;) Khengre, (1976) has noticed quite rapid production of NO_3 in the ammoniated-medium black soil studied. The data on changes in NH_4^+ and NO_3^- in soil solution presented in Tables 12 and 17 respectively also suggest nitrification of added NH_3 with time in both the soils. This indicates, that after 3-day incubation soil-solution EC appeared to be largely a function of (a) soluble cations exchanged and (b) nitrates produced in the ammoniated soils studied.

4.3 Measured concentration of cations in soil solution :

Measured concentrations of cations viz. Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} and NH_4^{+} (NH_4^{+} + NH_3) as influenced by levels of ammoniation and incubation time are given in Tables 7 through 14 and Fig. 6 through 13.

4.3.1 Calcium and Magnesium :

The measured concentration of Ca^{2+} and Mg^{2+} in check solutions were in the range of 10^{-3} to 10^{-2}M and did not show variation during 120-day incubation (Tables 7 and 8). Fig. 6 and 7 show that the trends in changes in measured concentration of Ca^{2+} in soil solution as affected by ammoniation levels and incubation were virtually similar to those in measured concentrations of Mg^{2+} in soil solution of the soils studied.

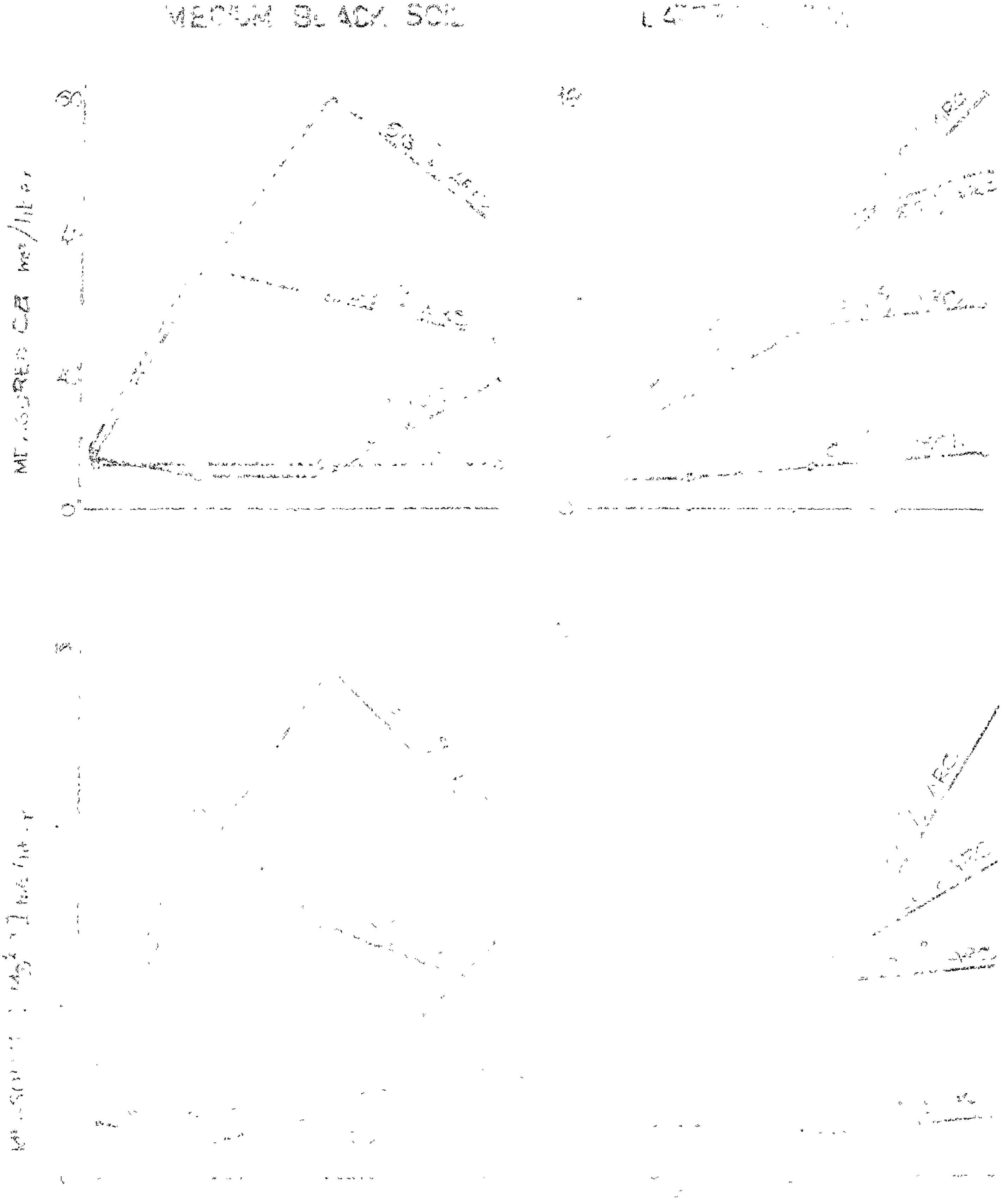
After 3-day incubation measured Ca^{2+} and Mg^{2+} ion concentrations did not significantly increase with increase in levels of ammoniation of the soil studied. These results suggest that probably negligible or small magnitude of exchange reaction might have occurred due to significant proportion of added NH_3 existing in undissociated or free NH_3 (aq) form (Table 13). Another possible reason is that high soil pH prevailing during 3-day incubation (Table 6) may have caused simultaneous precipitation of displaced Ca^{2+} and Mg^{2+} as carbonates (Du-Pleassis, and Kroontje, 1964, Russell, 1965).

Table 5: Measured and calculated concentrations of sodium and its activity in soil solution of the [illegible] black and [illegible] soils, as influenced by added anhydrous NH$_3$ and incubation time

NH$_3$ added ([illegible])	Incubation time (days)	Sodium					
		[illegible] black soil			[illegible] soil		
		concentration		Activity	concentration		Activity
		Measured	Calculated		Measured	Calculated	
		m mole/liter					
	3	2.31	2.54	1.76	0.55	0.52	0.40
	35	2.85	2.60	1.76	0.55	0.51	0.40
0 (check)	70	3.06	2.77	1.84	0.65	0.59	0.45
	120	3.05	2.75	1.83	0.70	0.64	0.50
	3	4.38	3.61	2.45	1.10	0.88	0.73
	35	17.23	16.59	7.48	2.59	2.44	1.54
33	70	15.04	14.40	6.61	3.60	3.48	2.03
	120	12.05	11.47	5.27	4.18	4.04	2.36
	3	4.14	3.39	2.26	1.15	0.89	0.69
	35	16.98	15.88	7.35	3.06	2.86	1.74
66	70	29.38	28.43	11.22	5.30	5.12	2.78
	120	20.64	19.17	8.62	5.63	5.46	3.40
	3	4.04	3.62	2.19	0.95	0.84	0.60
	35	2.71	2.08	1.49	2.81	2.53	1.61
100	70	2.59	2.18	1.38	4.50	4.29	2.40
	120	9.03	7.83	4.80	8.03	7.55	3.84

Table 9: Measured and calculated concentrations of magnesium and its activity in soil solution of the medium black and lateritic soils, as influenced by added anhydrous NH$_3$ and incubation time

NH$_3$ added ([illegible])	Incubation time (days)	Magnesium					
		Medium black soil			Lateritic soil		
		concentration		Activity	concentration		Activity
		Measured	Calculated		Measured	Calculated	
		mole/liter					
0 (check)	3	0.94	0.85	0.56	0.45	0.43	0.33
	35	0.95	0.87	0.50	0.40	0.38	0.30
	70	1.13	1.08	0.73	0.35	0.32	0.25
	120	1.26	1.15	0.78	0.38	0.35	0.23
33	3	1.50	1.40	0.88	0.80	0.74	0.55
	35	5.41	1.18	2.56	1.05	1.00	0.65
	70	3.53	3.32	1.67	1.70	1.64	1.00
	120	2.72	2.58	1.39	1.73	1.72	1.05
66	3	1.55	1.38	0.9[illegible]	0.65	0.60	0.42
	35	4.36	4.11	2.07	1.41	1.33	0.84
	70	7.29	7.05	3.17	1.85	1.80	1.00
	120	4.73	4.33	2.20	2.75	2.59	1.50
100	3	0.71	0.62	0.40	0.73	0.66	0.47
	35	0.47	0.35	0.27	1.32	1.29	0.79
	70	0.83	0.79	0.45	1.80	1.73	1.01
	120	3.44	3.02	1.90	4.25	4.11	2.13



6 : [illegible]

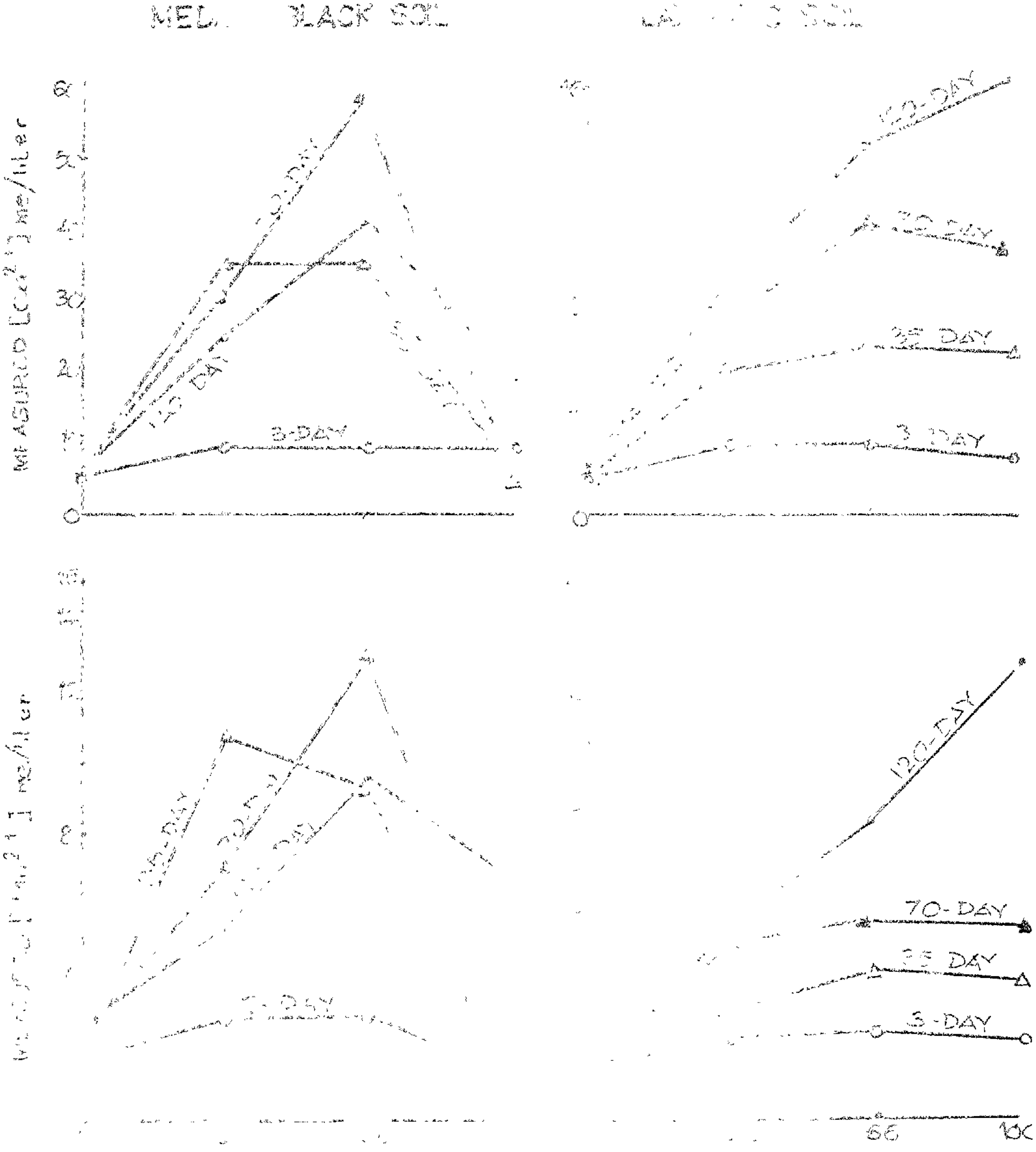
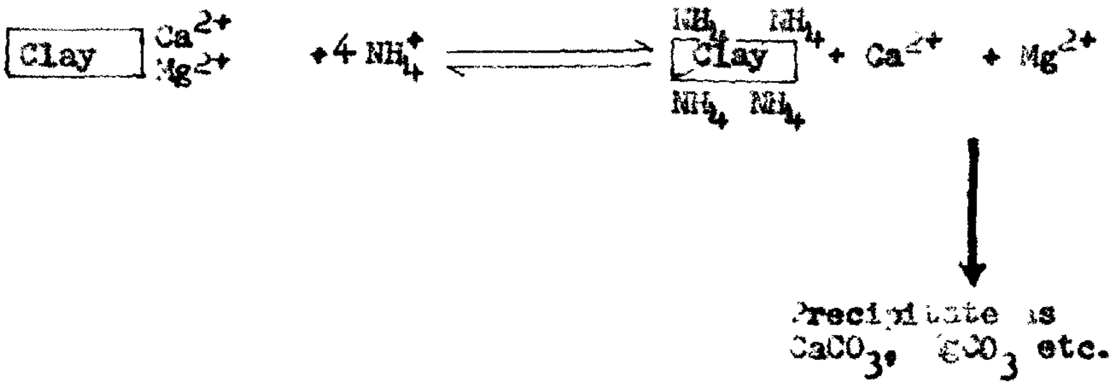


Fig 7 : [illegible] measured [illegible] soils.



$$\boxed{\text{Clay}}\begin{matrix}Ca^{2+}\\ Mg^{2+}\end{matrix} + 4\,NH_4^+ \rightleftharpoons \begin{matrix}NH_4 & NH_4\\ \multicolumn{2}{c}{\boxed{\text{Clay}}}\\ NH_4 & NH_4\end{matrix} + Ca^{2+} + Mg^{2+}$$

Precipitate as $CaCO_3$, $MgCO_3$ etc.

In so far as, effect of ammoniation of the soil on changes in measured Ca^{2+} and Mg^{2+} in soil solution as a function of time are concerned, the medium black soil showed distinctly different behaviour from the lateritic soil. The measured concentrations of Ca^{2+} and Mg^{2+} in soil solution of the medium black soil ammoniated at the 33 and 66 per cent ARC initially increased and tended to decerease toward the end of 120-day incubation, whereas that of 100% ARC, measured Ca^{2+} and Mg^{2+} concentration remained constant upto 70-day incubation and showed increase towards the end of 120-day incubation. On the other hand measured concentration of Ca^{2+} and Mg^{2+} in soil solution of lateritic soil ammoniated equal to 33, 66, and 100% ARC continued to increase throught-out 120-day experimental period. These changes in measured Ca^{2+} and Mg^{2+} in soil solution can be attributed partly to cation exchange. Decrease in NH_4OAc extractable Ca^{2+} and Mg^{2+} with added NH_3 and incubation time was noticed (Table 9).

Table 9 : Changes in NH_4OAC -extractable Ca and Mg contents of the ammoniated soils after extraction of soil solution with time

NH_3 added (% ARC)	Incubation time (days)	Medium black soil			Lateritic soil		
		Ca	Mg	Ca + Mg	Ca	Mg	Ca + Mg
		~~m-mole~~ meq/liter					
0 (check)	35	28.71	6.43	35.14	7.90	3.65	11.55
	70	29.11	7.31	36.42	7.75	3.65	11.40
	120	28.56	6.44	35.00	7.55	3.80	11.55
33	35	26.20	8.31	34.51	10.32	3.65	13.97
	70	29.39	5.11	34.50	6.68	3.04	9.72
	120	17.89	6.43	24.32	8.51	1.82	10.33
66	35	27.48	5.75	33.23	6.68	3.65	10.33
	70	26.84	3.83	30.67	5.47	3.04	8.51
	120	9.59	1.91	11.50	4.25	1.82	6.07
100	35	22.72	7.31	30.03	7.90	3.65	11.55
	70	26.84	5.11	31.95	4.50	3.65	8.15
	120	15.34	1.28	14.06	4.25	3.04	7.29

In the case of medium black soil, peak concentrations of Ca^{2+} and Mg^{2+} in soil solution were observed when it was ammoniated equal to 66% A.C and incubated upto 70-day period. In the case of lateritic soil, such peaks were not observed at any level of ammoniation studied during the 120-day incubation. These results indicate that the chemical nature of the sources of calcium and magnesium and processes determining the changes in measured Ca and Mg concentration in soil-solution were probably different in the medium black and in the lateritic soil studied.

4.3.2 Sodium and Potassium :

By and large the measured concentrations of Na^+ in soil solution increased with increasing levels of ammoniations and incoeasing incubation periods upto 70-days but showed decreasing trends thereafter. Exchange reactions appear to be largely responsible for these changes in Na^+ in soil solution.

$$\text{clay} \; Na + NH_4^+ \rightleftharpoons \text{clay} \; NH_4^+ + Na^+$$

As the concentration of NH_4^+ ions might have decreased with time (Table 12) owing to nitrification, the displaced Na^+ ions probably were readsorbed on soil colloidal clay complex by making the exchange reaction occur in opposite direction before reaching equilibrium.

Table 10: Measured and calculated sodium concentration and its activity in soil solution of medium black and lateritic soils as influenced by added anhydrous NH_3 and incubation time

NH_3 added (% AHC)	Incubation time (days)	Sodium			
		Medium black soil		Lateritic soil	
		Measured conc.	activity	measured conc.	activity
		m M			
0 (check)	3	1.65	1.52	0.63	0.58
	35	1.78	1.57	0.78	0.72
	70	1.87	1.57	0.83	0.76
	120	2.00	1.75	0.78	0.71
33	3	2.09	1.79	0.52	0.47
	35	3.52	2.89	1.30	1.13
	70	3.26	2.62	1.70	1.46
	120	2.00	1.64	1.48	1.27
66	3	1.96	1.67	0.65	0.57
	35	3.91	3.11	1.91	1.65
	70	4.78	3.66	2.00	1.68
	120	2.78	2.19	1.80	1.51
100	3	1.86	1.58	0.55	0.43
	35	2.17	1.73	1.39	1.20
	70	1.96	1.58	1.81	1.53
	120	2.52	1.89	1.50	1.07

Table 11 : Measured and calculated potassium concentration and its activity in the soil solution of the medium black and lateritic soils, as influenced by added anhydrous NH_3 and incubation time

NH_3 added (% ARC)	Incubation time (days)	Potassium			
		Medium black soil		Lateritic soil	
		measured conc.	activity	measured conc.	activity
		m mole/liter			
0 (check)	3	0.08	0.07	0.07	0.07
	35	0.08	0.07	0.07	0.07
	70	0.09	0.08	0.09	0.08
	120	0.09	0.08	0.08	0.07
33	3	0.10	0.08	0.09	0.08
	35	0.12	0.09	0.25	0.22
	70	0.13	0.10	0.28	0.24
	120	0.10	0.08	0.13	0.11
66	3	0.13	0.11	0.10	0.09
	35	0.14	0.11	0.38	0.32
	70	0.18	0.13	0.49	0.41
	120	0.10	0.08	0.30	0.25
100	3	0.15	0.13	0.10	0.09
	35	0.18	0.15	0.56	0.48
	70	0.21	0.17	0.58	0.48
	120	0.13	0.11	0.43	0.35

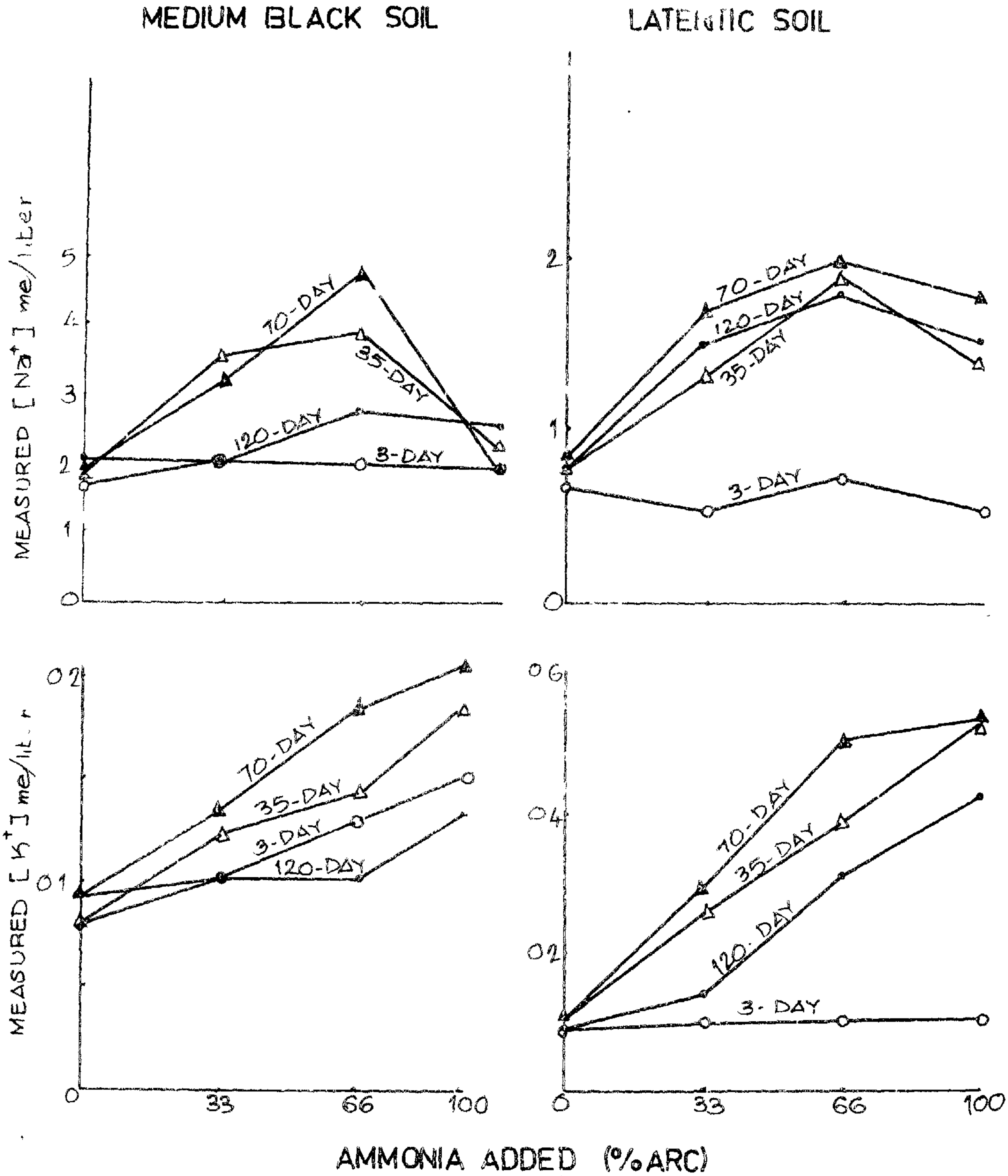


Fig 9 : Changes in measured Na$^+$ and K$^+$ concentrations in soil solution of the incubated soils as influenced by added anhydrous ammonia.

For unknown reasons however, changes in measured concentrations of Na^+ in soil solutions of the medium black soil, ammoniated equal to 100% ARC were different from those of other two ammoniation levels.

As regards the changes in measured concentrations of K^+ ion in soil solution, trends were as per expections. It is well known that ionic size of K resembles that of NH_4^+ (Marshall, 1964), and hence their exchange behaviour is also similar. Probably therefore increase in measured K^+ concentration was noticed in soil solution with increase in addition of ammonia to the medium black and lateritic soils. Amount of K in soil solution decreased after 75-day incubation and can be explained as follows: Due to nitrification process NH_4^+ ion on the soil exchange may have decreased (Table 12) therefore, K ions may have been readsorbed by soil-solid phase.

4.3.3 Ammonium :

The measured NH_4^+ ion concentration in soil solution increased when ammoniation levels increased from 0 to 100% ARC in both the soils (Table 12 Fig. 10 and 11). Under favourable conditions the NH_4^+ ions in soil are oxidised to nitrates by nitrifying bacteria (Frederik and Broadbent 1966). Secondly soil micro-organisms are reported to utilize ammonium ions resulting in their immobilization (Janson *et al.*, 1965 and Jansson , 1958).

Table 13: Measured and calculated concentration of NH_3 and its activity in soil solution of the medium black and lateritic soils, as influenced by added anhydrous NH_3 and incubation time

NH_3 added (% ARC)	Incubation time (days)	Ammonium					
		Medium black soil concentration		Activity	Lateritic soil concentration		Activity
		measured	calculated		measured	calculated	
		m mole/liter					
0 (check)	3	1.10	1.09	0.96	1.80	1.79	1.66
	35	1.01	1.00	0.88	1.80	1.79	1.66
	70	1.30	1.29	1.01	1.85	1.84	1.69
	120	1.30	1.29	1.01	1.85	1.84	1.69
33	3	7.60	7.56	6.42	6.00	5.96	5.36
	35	3.08	3.06	2.37	3.80	3.78	3.28
	70	3.10	3.09	2.42	3.22	3.21	2.73
	120	4.50	4.48	3.59	4.66	4.59	3.90
66	3	12.40	12.29 10.03	10.03	7.80	7.75	6.75
	35	5.00	4.96	3.85	6.40	6.36	5.44
	70	4.00	3.98	2.91	6.19	6.17	5.10
	120	6.60	6.57	5.00	6.67	6.65	5.60
100	3	15.50	15.53	12.93	10.30	10.21	9.05
	35	14.00	13.69	11.74	9.30	9.22	7.92
	70	13.50	13.29	11.19	8.12	8.09	6.74
	120	10.15	10.02	8.41	10.15	10.12	8.11

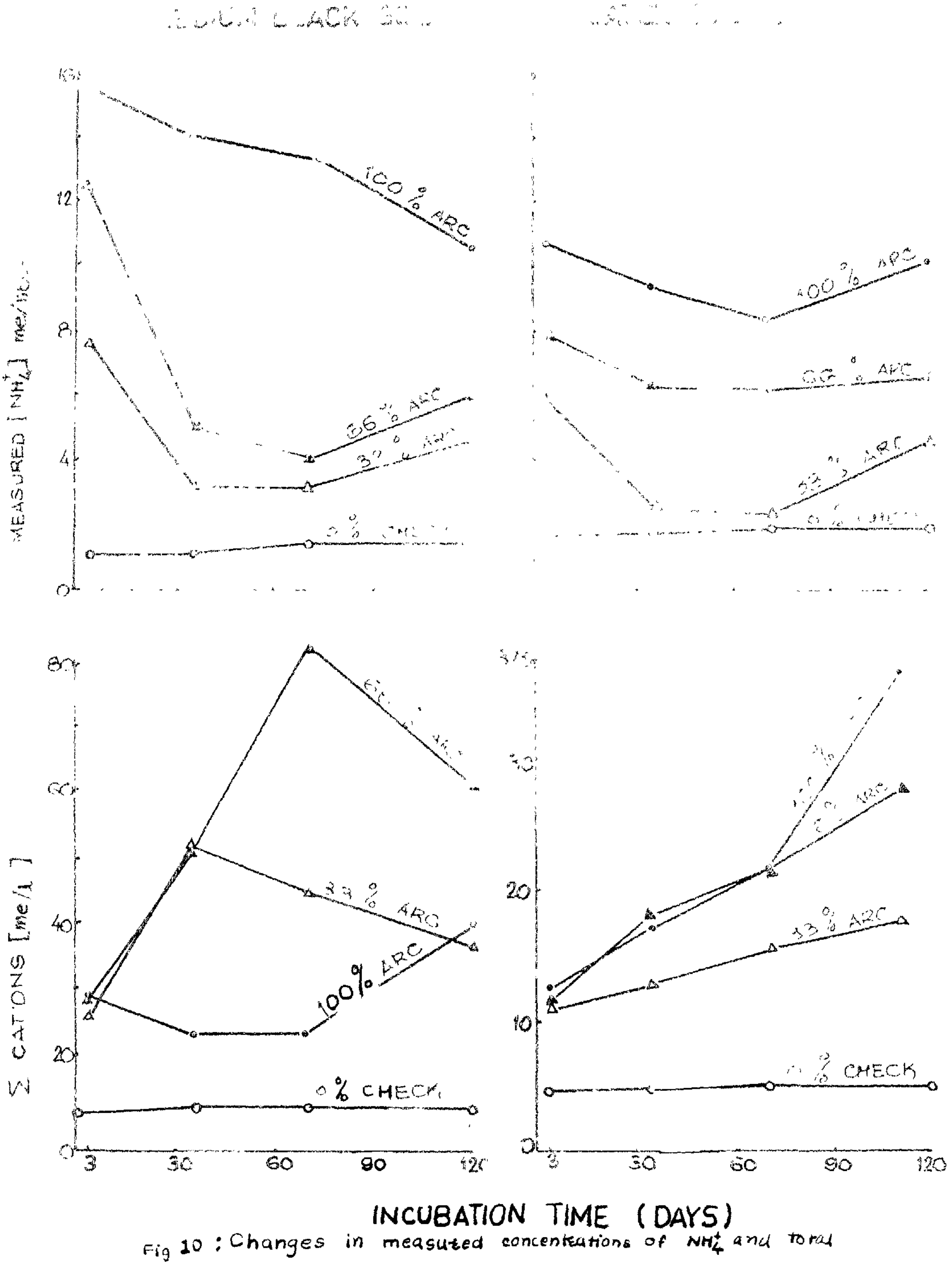
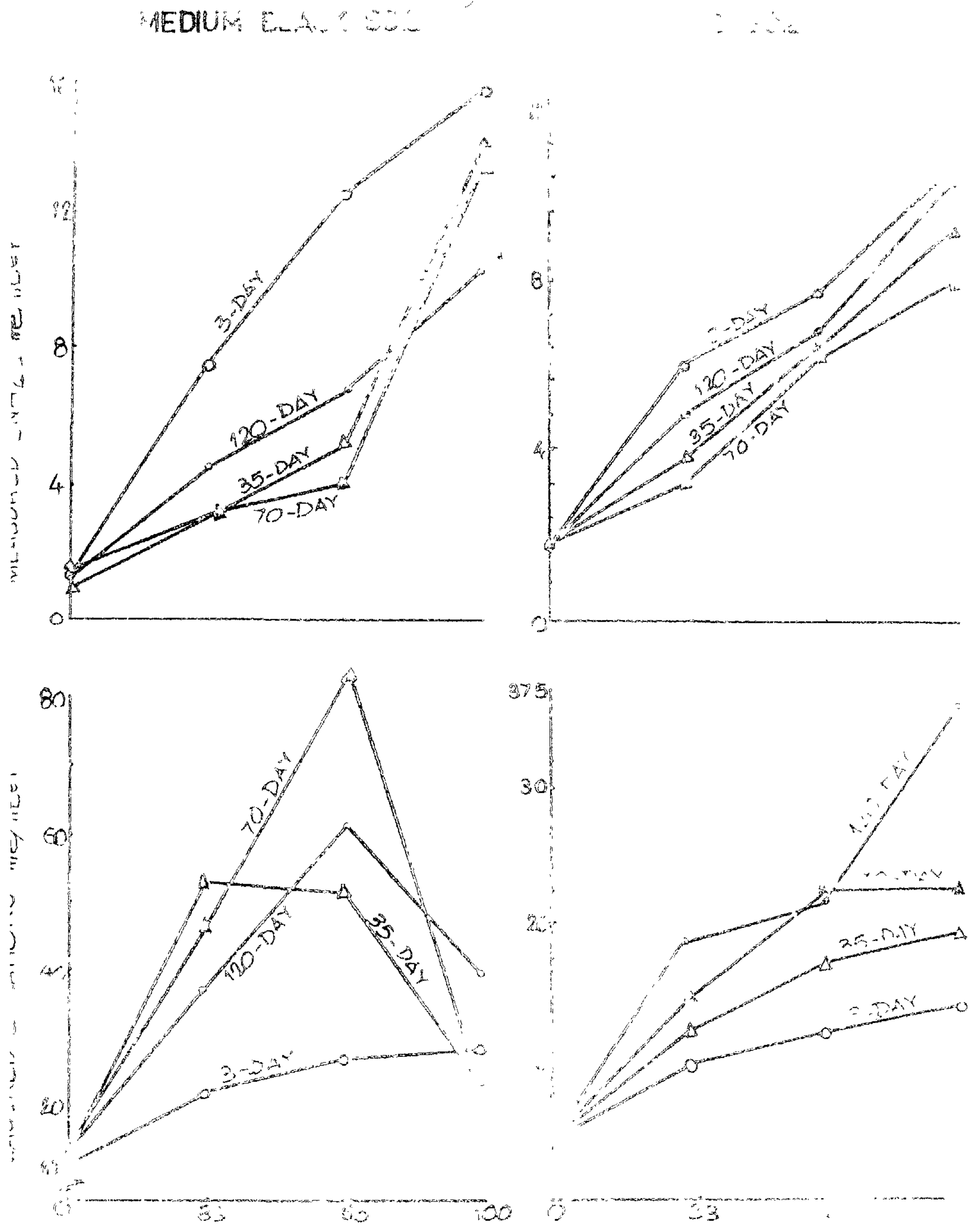


Fig 10 : Changes in measured concentrations of NH_4^+ and total cations in soil solution of ammoniated soils as influenced by added anhydrous ammonia.


MEDIUM BLACK SOIL
3-DAY
120-DAY
35-DAY
70-DAY
0
4
8
12
16
0
4
8
0
20
40
60
80
375
30
20
0
33
66
100
33

11 [illegible]

Nitrification of added anhydrous NH_3 in the vertisol studied at approximate field capacity has been reported by Khengre (1976) . The data reported in Table 17 and 18 also clearly suggest, that there was increase in NO_3^- concentration in soil solution. It can therefore, be said that nitrification of NH_4^+ was largely responsible for decrease in measured NH_4^+ concentration in soil solution of the ammoniated soils. In the case of medium black soil ammoniated equal to 100% ARC, the decrease in NH_4^+ - N appeared to be rather slow probably due to lesser rate of nitrification. (Table 17 and 18, Fig. 16 and 17). Khengre (1976) also noticed "delay phase" during nitrification of ammonia in the vertisol to which ammonia was added equal to 100% ARC, probably due to partial sterilization effect (Aleem and Alexander, 1960).

In the case of lateritic soils, the rate of nitrification being slow, probably because of its unfavourable soil pH, the decrease in measured NH_4^+ ion concentration in its soil solution was rather slow. This is also supported by the data on changes in measured NO_3^- concentration in its soil solution (Table 17 and 18). Khengre (1976 personal communication) observed very slow rate of nitrification in the ammoniated lateritic soil.

Table 13 : Changes in undissociated NH_3 in soil solution, as influenced by added anhydrous ammonia with incubation time

Ammonia added (% ARC)	Incubation time	Medium black soil	Lateritic soil
		m mole/liter	
33 %	3	1.65	0.15
	35	0.03	0.03
	70	0.03	0.01
	120	0.05	0.03
66	3	3.22	0.21
	35	0.09	0.04
	70	0.01	0.01
	120	0.03	0.01
100	3	4.75	0.35
	35	0.25	0.10
	70	0.13	0.02
	120	0.06	0.02

* Calculated according to the method suggested by Bezdicek *et al.*, (1971).

The measured NH_4^+ concentration includes undissociated or free NH_3 (aq). As free NH_3(aq) is toxic to plants, as well as soil micro-organisums, an attempt was made to calculate free NH_3(aq) using the method of calculation suggested by (Bezdicek at al., 1971) . The calculated free or undissociated NH_3(aq) concentrations in soil solution of both the ammoniated-soils are given in Table 13. It is apparent from the data that free NH_3(aq) concentration ranged from 0.01 to 4.75 mM/liter in soil solution of soils studied. After 3-day incubation, free NH_3(aq) was maximum; however it decreased rapidly with incubation time, probably due to protonation reaction and/or subsequent chemical sorption (Mortland, 1966). These data confirm the observations made by Parr and Papendick (1966), and probably explain the changes in soil-solution pH and measured NH_4^+ concentration in soil solution.

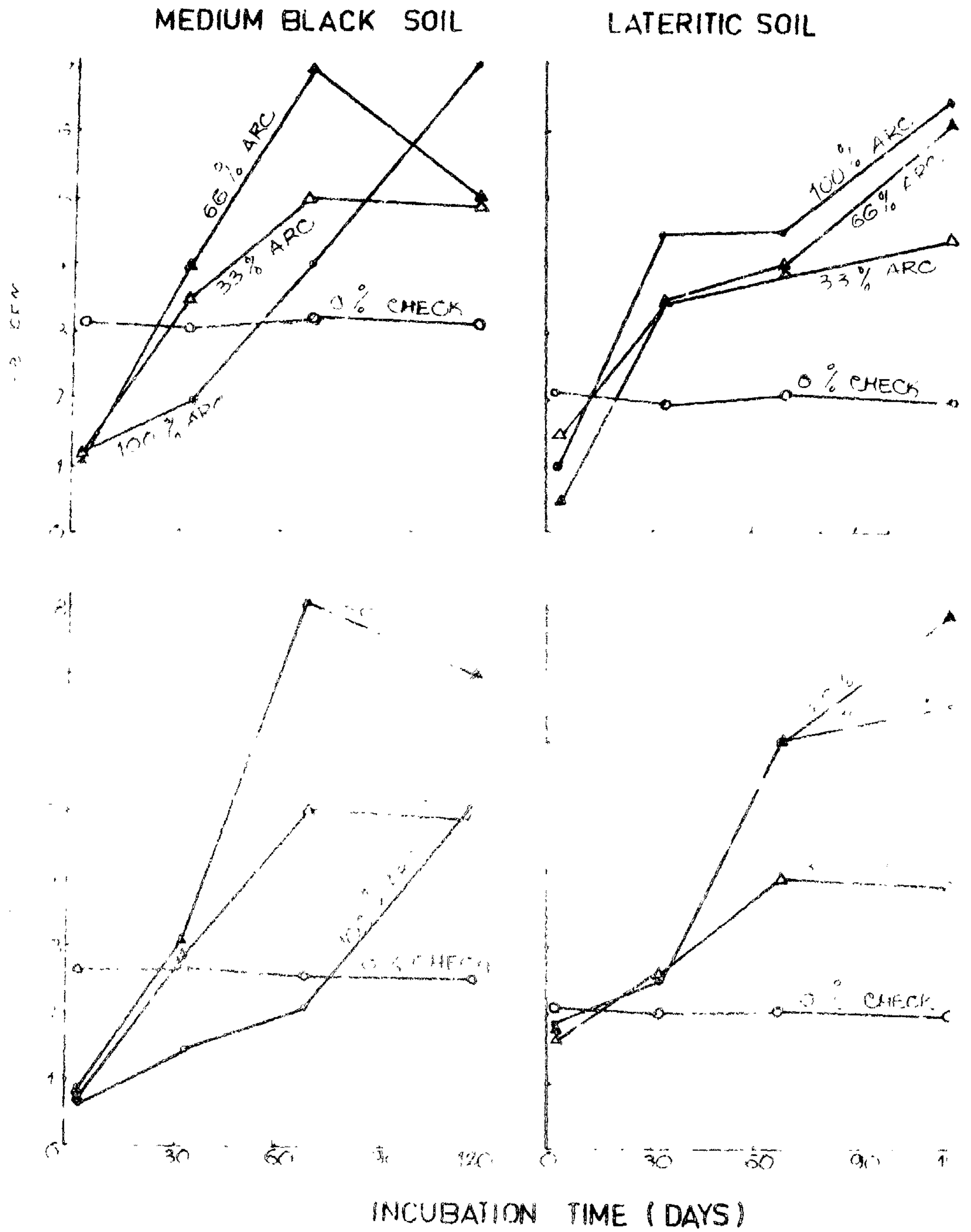
4.3.4 Iron and Manganese :

The data on effects of addition of anhydrous NH_3 to the medium black and latritic soils on measured concentration of Fe and Mn in soil solution at different periods of incubation are presented in Table 14 .

It is apparent from the Fig. 12 and 14, that after 3-day incubation time, measured concentration of Fe and Mn decreased with increase in ammoniation levels in both the soils. This was possibily due to rise in soil-solution pH, eventually resulting in decreased solubility of Fe and Mn compunds and/or increased stability of Fe and Mn complexes (Schnitzer and Khan, 1971).

Table 14 : Measured concentration of Fe and Mn in soil solution of medium black and lateritic soils, as influenced by added anhydrous NH_3 with time

NH_3 added (%ARC)	Incubation time (days)	Medium black soil		Lateritic soil	
		Fe	Mn	Fe	Mn
–		ppm			
	3	3.20	2.70	2.10	2.06
0 (check)	35	3.10	2.75	1.95	1.98
	70	3.30	2.70	2.15	2.00
	120	3.25	2.70	2.00	1.95
	3	1.20	0.95	1.50	1.70
33	35	3.40	2.95	3.40	2.60
	70	4.90	5.00	4.10	3.85
	120	4.90	4.80	5.30	3.70
	3	1.10	1.00	0.50	1.80
33	35	3.90	3.00	3.40	2.50
66	70	6.90	8.02	4.20	5.93
	120	5.00	7.01	6.00	8.00
	3	1.25	0.90	1.00	1.90
	35	1.80	1.50	4.50	2.50
100	70	3.70	2.00	4.55	5.95
	120	7.01	4.94	6.49	6.21


MEDIUM BLACK SOIL
LATERITIC SOIL
66 % ARC
33 % ARC
100 % ARC
0 % CHECK
100 % ARC
66 % ARC
33 % ARC
0 % CHECK
0 % CHECK
0 % CHECK
30
60
120
0
30
50
90
INCUBATION TIME (DAYS)

12 :

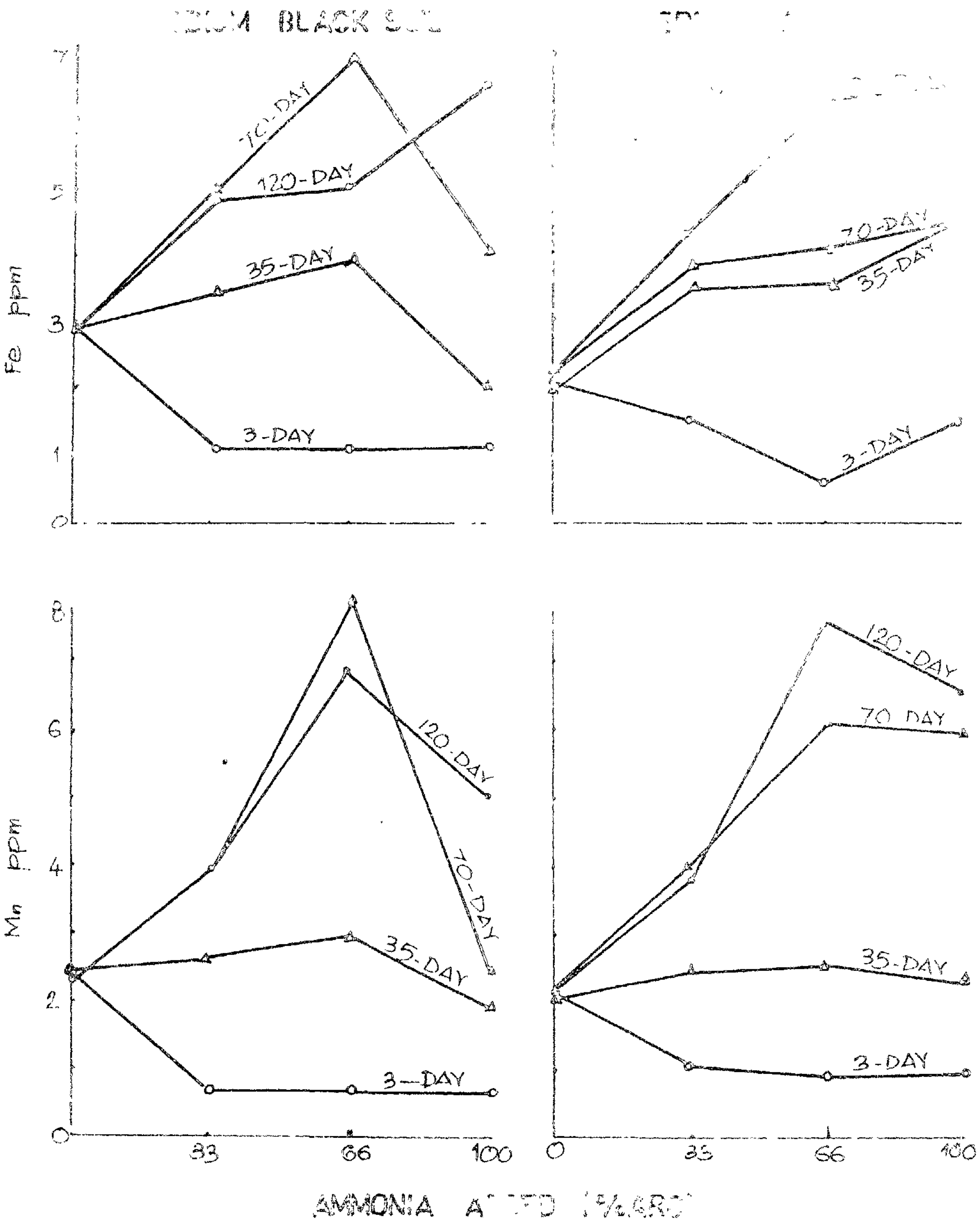


Fig 13: Changes in measured iron and mangaese concentrations in soil solution of the incubated soil as influenced by added anhydrous ammonia.

However, as incubation period progressed the acidifying effects of nitrification of added NH_3 were observed (Table 18), the lowering of soil-solution pH seemed to have, in general, increased Mn and Fe in soil solution. McDowell and Smith (1958) measured Mn concentration in saturation extract of ammonia-treated soil, and noticed 5 to 6 times more Mn than that found in the soil receiving no ammonia as a result of the increased H^+ ion activity (Stevens and Reuss 1975). While studying the effects of NH_3 on chemical properties of a temparate calcareous soil, Stevens and Reuss (1975) noticed DTPA-extractable Mn was higher near the injection point of the NH_3.

4.4 Measured concentrations of anions in soil solution :

The data on changes in measured concentrations of anions namely CO_3^{2-}, HCO_3^- , Cl^-, NO_3^- , SO_4^{2-} and phosphate in soil solution as influenced by increasing levels of ammoniation of the soils studied are given in Table 15 through 20 and presented in Fig 14 through 19 .

4.4.1 Carbonate and bicarbonate :

Insofar as CO_3^{2-} ions are concerned, they were found in the ammoniated medium black soil after 3-day incubation only and their concentration in soil solution increased with increasing levels of ammoniation i.e. from 3% to 100% MRC. This may be due to soil-solution pH being 8.4 (Table 6 and Fig 5). As soon as soil-solution pH dropped as a result of nitrification (Table 18 and Fig. 16) carbonate could not be

Table 15 : Measured and calculated concentrations of CO_3^{2-} and HCO_3^- and their activities in soil solutions of medium black soil as influenced by added anhydrous NH_3 with time

NH_3 added ([illegible])	Incubation time (days)	Medium black soil				
		Carbonates		Bicarbonates		
		Measured conc.	Activity	Concentration		Activity
				Measured	Calculated	
		mmole/liter				
0 (check)	3	ND	-	0.70	[illegible]	0.65
	35	-	-	0.90	[illegible]	0.79
	70	-	-	1.30	[illegible]	1.14
	120	-	-	1.10	[illegible]	0.96
33	3	0.40	0.21	1.80	1.71	1.54
	35	-	-	0.48	0.42	0.38
	70	-	-	0.40	0.35	0.32
	120	-	-	1.10	0.99	0.91
66	3	0.50	0.25	2.20	[illegible]	1.87
	35	-	-	0.60	[illegible]	0.48
	70	-	-	0.45	0.35	0.34
	120	-	-	1.21	1.03	0.95
100	3	0.55	0.34	[illegible]	[illegible]	2.21
	35	-	-	1.70	1.55	1.45
	70	-	-	1.02	[illegible]	[illegible]
	120	-	-	0.99	[illegible]	0.84

ND = not detected

Table 15 : Measured and calculated concentrations of $CO_3^{=}$ and HCO_3^- and their activities in soil solution of lateritic soil as influenced by added anhydrous NH_3 with time

NH_3 added ([illegible])	Incubation time (days)	Lateritic soil		
		Bicarbonate		
		Concentration		Activity
		Measured	Calculated	
		mmole/liter		
	3	0.50	0.50	0.46
	35	0.54	0.54	0.50
0 (check)	70	0.60	0.60	0.55
	120	0.69	0.69	0.63
	3	1.20	1.16	1.08
	35	0.90	0.87	0.78
33	70	0.45	0.43	0.39
	120	0.69	0.65	0.59
	3	1.60	1.57	1.40
	35	1.00	0.96	0.86
66	70	0.55	0.52	0.45
	120	0.60	0.56	0.50
	3	2.20	2.17	2.00
	35	1.20	1.16	1.04
100	70	0.45	0.42	0.38
	120	0.64	0.58	0.52

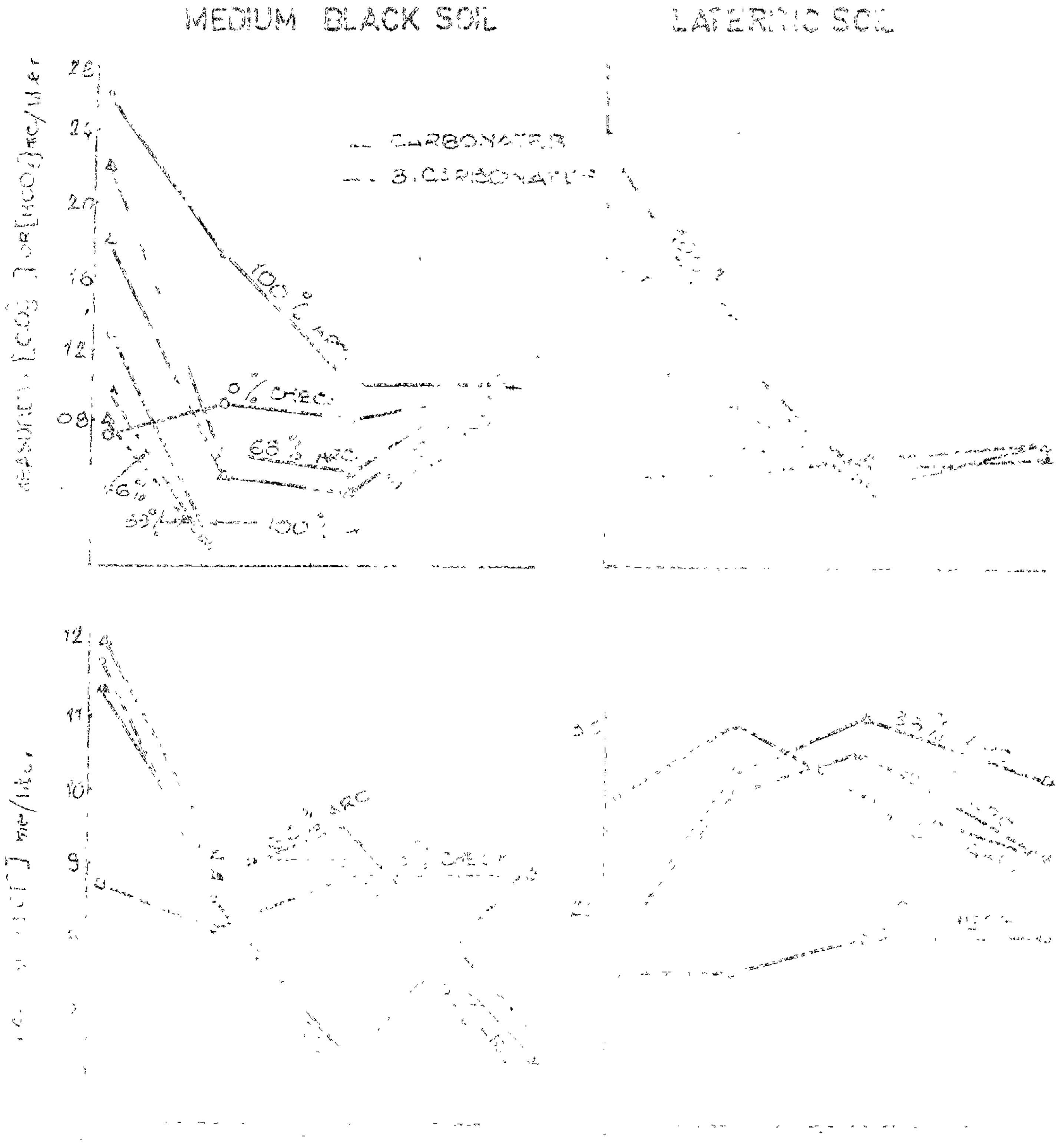
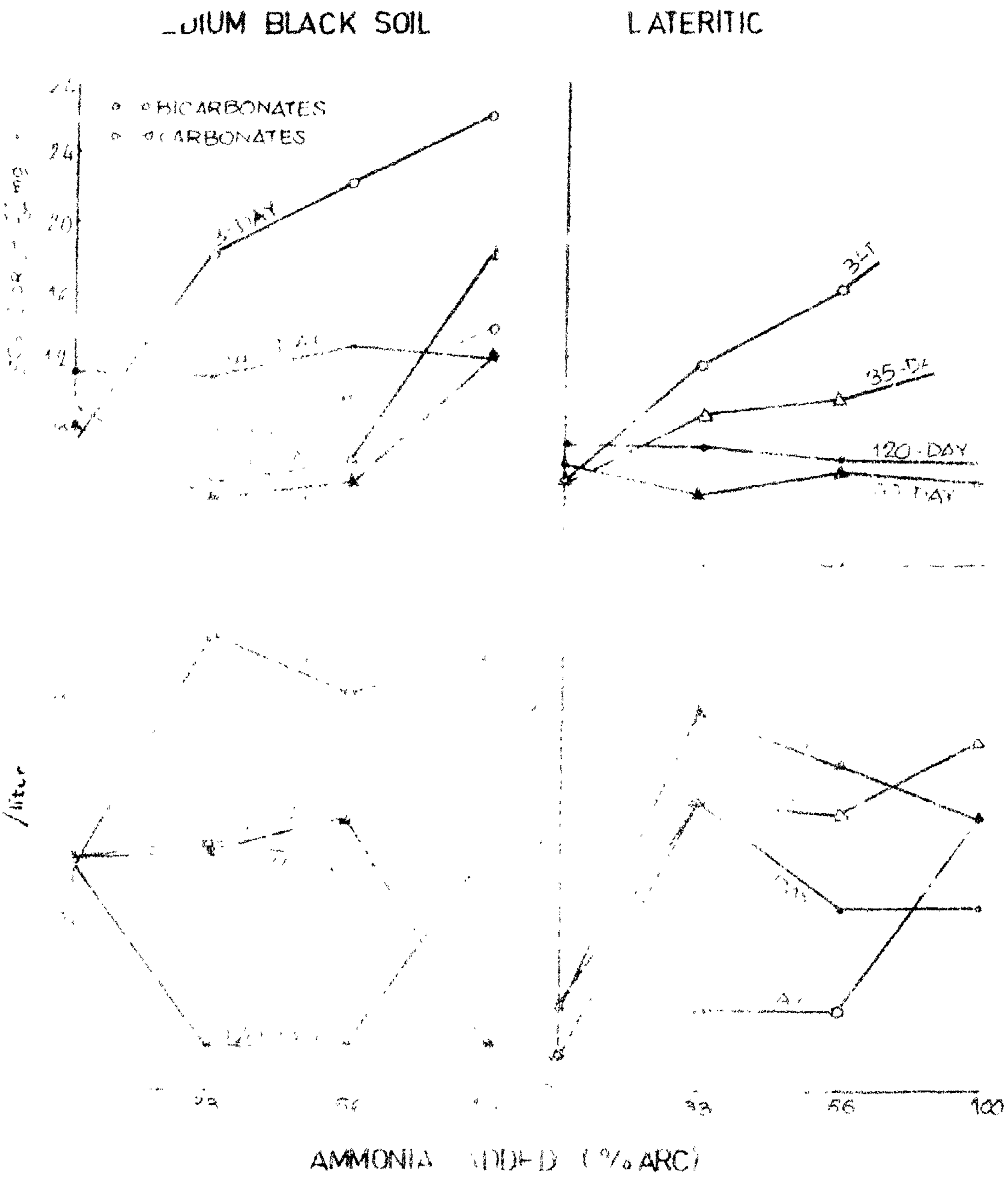


Fig 14 : Changes in measured CO_3^{2-}, HCO_3^- and Cl concentrations in soil solution of the ammoniated soils as influenced by incubation time.



[illegible] in measured [illegible], [illegible] concentrations in [illegible] soil solution of the [illegible] soils.

Carbonate ions were not at all found in soil solution of ammoniated lateritic soil during 120-day incubation period.

As regards HCO_3^- in soil solution, its concentration increased with increasing ammoniation levels in both the soils after 3-day incubation. With nitrification of ammonium in soil solution apparent increase in H^+ ion activity might have decreased measured HCO_3^- ion concentration in soil solution of the ammoniated soils with time i.e. after 3-day incubation.

4.4.2 Chloride :

The measured concentration of Cl^- in soil solution increased with increasing levels of ammoniation of the soils studied after 3-day incubation (Table 17 and Fig 15). The changes in concentration of Cl^- in soil solution of ammoniated soils did not show any definite trend with time (Fig. 14). Chloride ions exhibit negative adsorption phenomenon at soil solid-solution interface . No satisfactory explanation can be given for the changes in Cl^- concentration in soil solution of the ammoniated soils with time.

4.4.3 Nitrate :

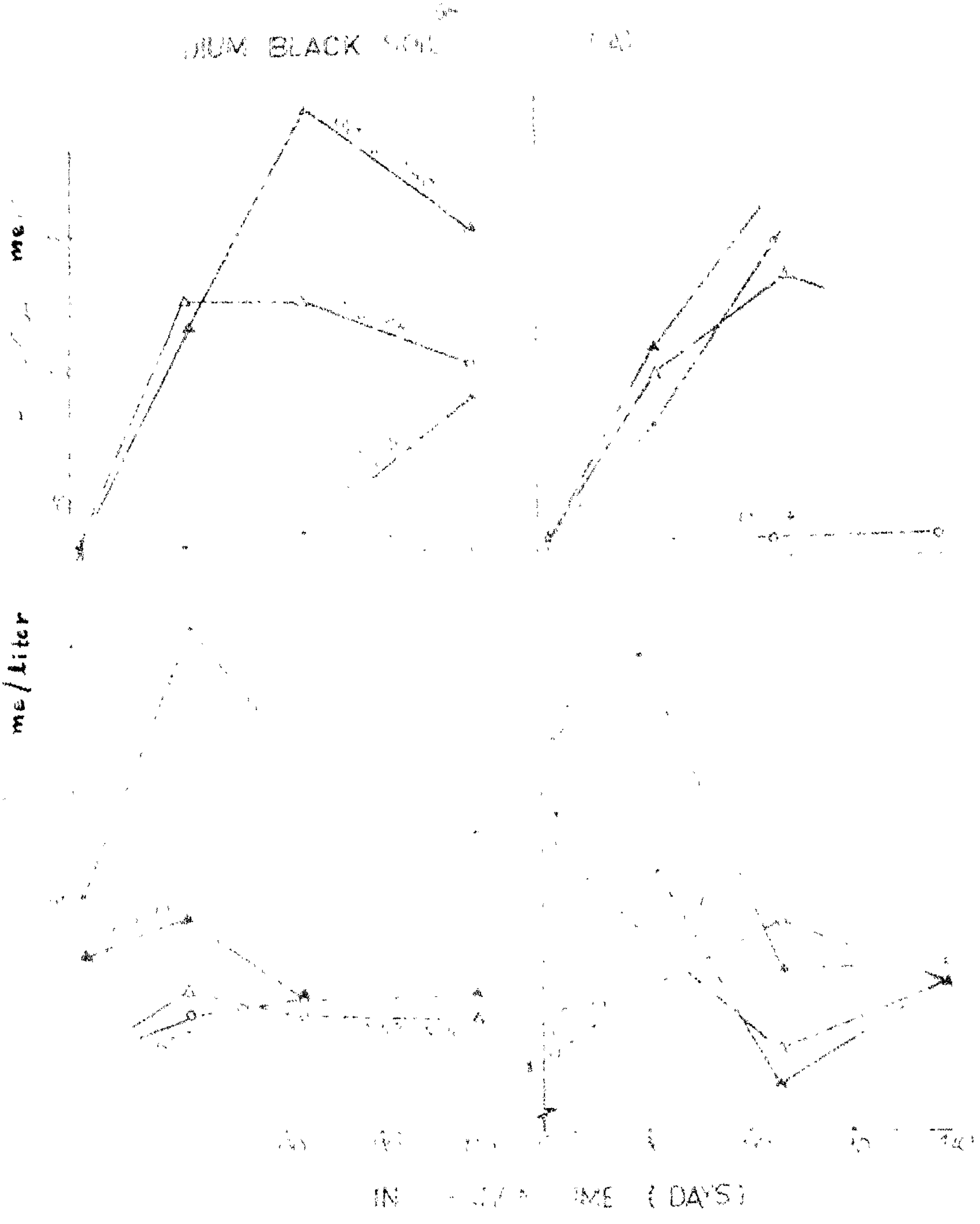
Figures 16 and 17 show that the NO_3^- ion concentration in soil solution increased with increasing levels of ammoniation and with incubation time in both the soils studied. This was attributed to nitrification of ammonium ions in solution of the ammoniated soils. Production of nitrates

Table 17 : Measured concentration of $\overline{Cl}$ with its activities in soil solution of the soil studied as influenced by added anhydrous NH_3 and incubation time

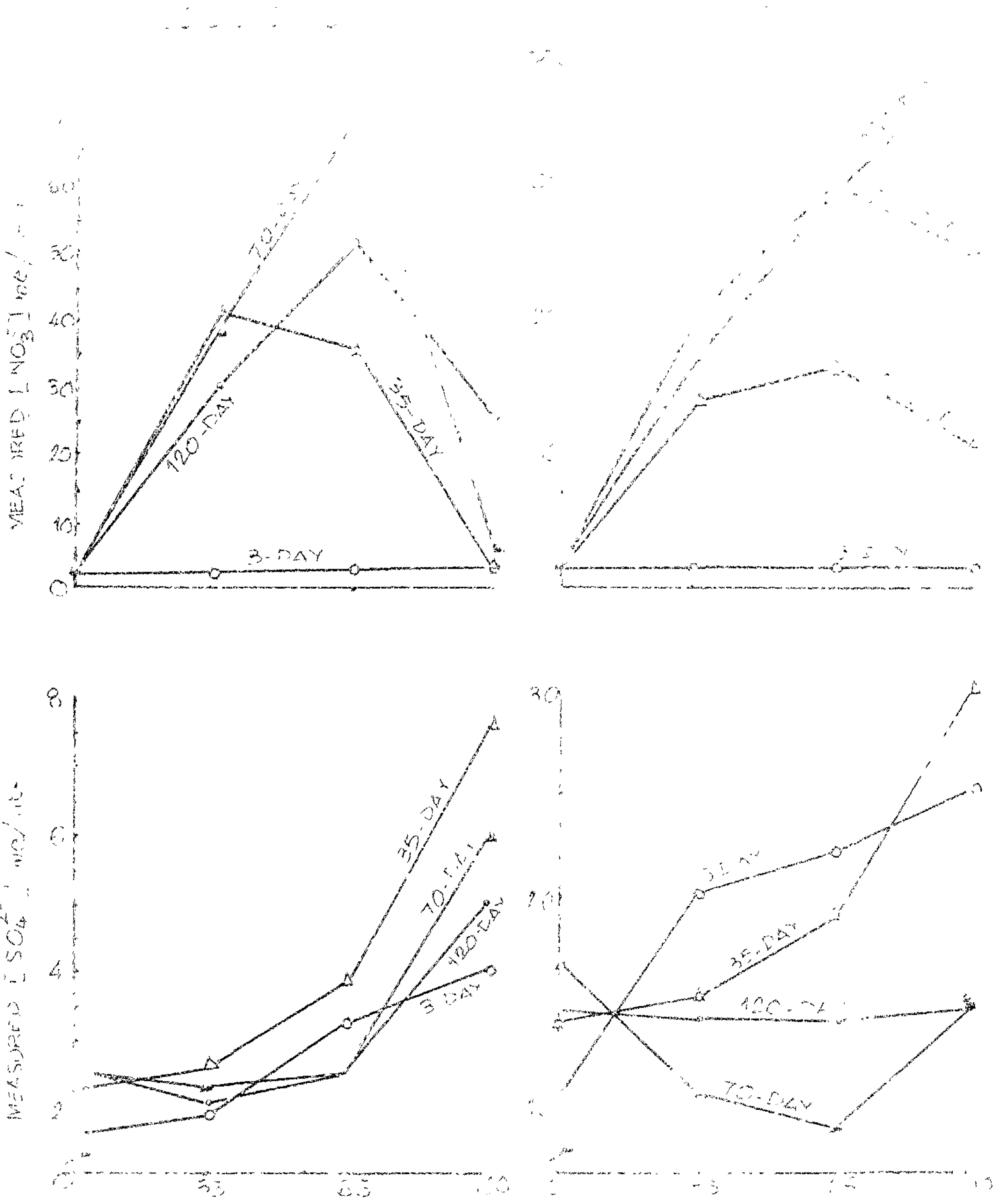
NH_3 added (% [illegible]C)	Incubation time (days)	Chloride			
		Medium black soil		Lateritic soil	
		Measured concentration	activity	measured concentration	activity
		m mole			
(0) (check)	3	8.66	7.60	1.60	1.47
	35	8.02	7.01	1.63	1.50
	70	8.82	7.65	1.80	1.54
	120	8.82	7.65	1.80	1.64
33	3	11.97	10.87	1.80	1.61
	35	9.04	7.02	2.70	2.33
	70	8.92	7.02	3.00	2.62
	120	6.30	5.06	2.70	2.30
66	3	11.34	10.71	1.80	1.56
	35	8.63	6.86	2.60	2.22
	70	9.45	6.99	2.86	2.37
	120	6.30	4.82	2.25	1.86
100	3	11.71	10.73	2.60	2.28
	35	8.48	7.15	2.97	2.54
	70	6.30	5.25	2.60	2.17
	120	9.00	7.49	2.25	1.59

Table 18 : Measured concentration of NO_3^- with its activities in soil solution of soil studied as influenced by added anhydrous NH_3 and incubation time

NH_3 added ([illegible])	Incubation time (days)	Nitrate			
		Medium black soil		Lateritic soil	
		measured conc.	activity	measured conc.	activity
		m mole/liter			
0 (check)	3	2.00	1.75	1.60	1.47
	35	1.91	1.67	1.60	1.47
	70	2.30	2.00	1.80	1.64
	120	2.30	2.00	1.84	1.68
33	3	2.70	2.29	1.60	1.43
	35	39.16	30.40	13.82	11.96
	70	38.26	30.10	20.09	16.99
	120	29.03	23.31	17.02	14.46
66	3	2.30	1.93	1.70	1.48
	35	35.06	27.2[illegible]	16.94	14.42
	70	68.59	50.51	28.58	23.78
	120	50.10	38.34	27.92	22.77
100	3	2.20	1.84	1.60	1.40
	35	2.48	2.09	10.31	9.23
	70	4.76	3.91	24.62	20.52
	120	24.38	20.30	36.91	29.68



BLACK
me
me/liter
(DAYS)



[illegible] **17.** [illegible] soil solution of [illegible] soil [illegible] nhydrous [illegible].

in a typical ammoniated and incubated vertisol of the Maharashtra State has been noticed by Khengre (1976) . After 70-day incubation period, however there was slight reduction in measured NO_3^- ion concentration in soil solution in the case of 33 and 66% ammoniation levels. This may be due to immobilization of nitrates present in soil solution by soil microorganisums and/or chemical denitrification (Pang 1975).

4.4.4 Sulphate :

With increase in levels of ammoniation of the soils, measured concentration in SO_4^{2-} ion in soil solution increased after 3-day incubation,but subsequently it tended to decrease, reaching original concentration in soil solution of the check soils (Fig. 16 and 17) . The probable reasons for these observation are not known.

4.4.5 Phosphate :

After 3-day incubation as activity of H^+ ion declined (Table 6), the calculated HPO_4^{2-} ion concentration increased and that of $H_2PO_4^-$ decreased in soil solution with increasing levels of ammoniation (Fig 18 and 19). However, with time nitrification occurred, soil-solution pH decreased, and as a result, calculated HPO_4^{2-} ion concentration decreased,whereas $H_2PO_4^-$ increased in soil solution in the case of ammoniated medium black soil. The changes in measured total P, and its distribution in HPO_4 and H_2PO_4 in soil solution of ammoniated

Table 19 : Measured and calculated concentrations of SO_4^{-} with its activities in soil solution of medium black and lateritic soils as influenced by added anhydrous NH_3 with time

NH_3 added ([illegible])	Incubation time (days)	Sulphate					
		Medium black soil concentration			Lateritic soil concentration		Activity
		Measured	Calculated		Measured	Calculated	
		m mole/liter					
0 (check)	3	0.80	0.58	0.49	0.52	0.45	0.37
	35	1.14	0.84	0.68	0.69	0.62	0.50
	70	1.25	0.90	0.72	0.84	0.74	0.54
	120	1.25	0.89	0.72	0.72	0.64	0.54
33	3	0.96	0.61	0.51	1.04	0.87	0.71
	35	1.31	0.85	0.51	0.78	0.53	0.45
	70	1.15	0.54	0.47	0.53	0.35	0.28
	120	1.12	0.49	0.49	0.50	0.32	0.27
66	3	1.66	1.05	0.85	1.11	0.94	0.60
	35	1.91	0.97	0.74	0.96	0.68	0.52
	70	1.25	0.13	0.41	0.44	0.26	0.21
	120	1.25	0.29	0.45	0.45	0.23	0.22
100	3	2.02	1.36	1.01	1.30	1.06	0.80
	35	14.03	3.99	2.99	1.51	1.08	0.83
	70	3.30	2.23	1.43	0.73	0.47	0.37
	120	2.50	2.04	1.27	0.73	0.33	0.32

Table 2[illegible] : Changes in calculated concentration of $H_2PO_4^-$ and $HPO_4^=$ in soil solution of medium black and lateritic soils as influenced by added anhydrous ammonia and incubation time

NH_3 added ([illegible])	Incubation time (days)	Phosphate			
		Medium black soil		Lateritic soil	
		$H_2PO_4^-$	HPO_4	H_2PO_4	HPO_4
		m mole/liter			
0 (check)	3	0.003	0.003	0.005	0.002
	35	0.003	0.005	0.006	0.003
	70	0.004	0.007	0.007	0.004
	120	0.003	0.005	0.004	0.002
33	3	0.001	0.013	0.003	0.008
	35	0.007	0.006	0.008	0.006
	70	0.007	0.006	0.009	0.004
	120	0.004	0.005	0.004	0.003
66	3	0.001	0.027	0.004	0.013
	35	0.005	0.010	0.007	0.006
	70	0.007	0.004	0.012	0.002
	120	0.007	0.004	0.006	0.002
100	3	0.002	0.098	0.005	0.018
	35	0.014	0.056	0.019	0.017
	70	0.012	0.016	0.011	0.005
	120	0.014	0.009	0.005	0.002

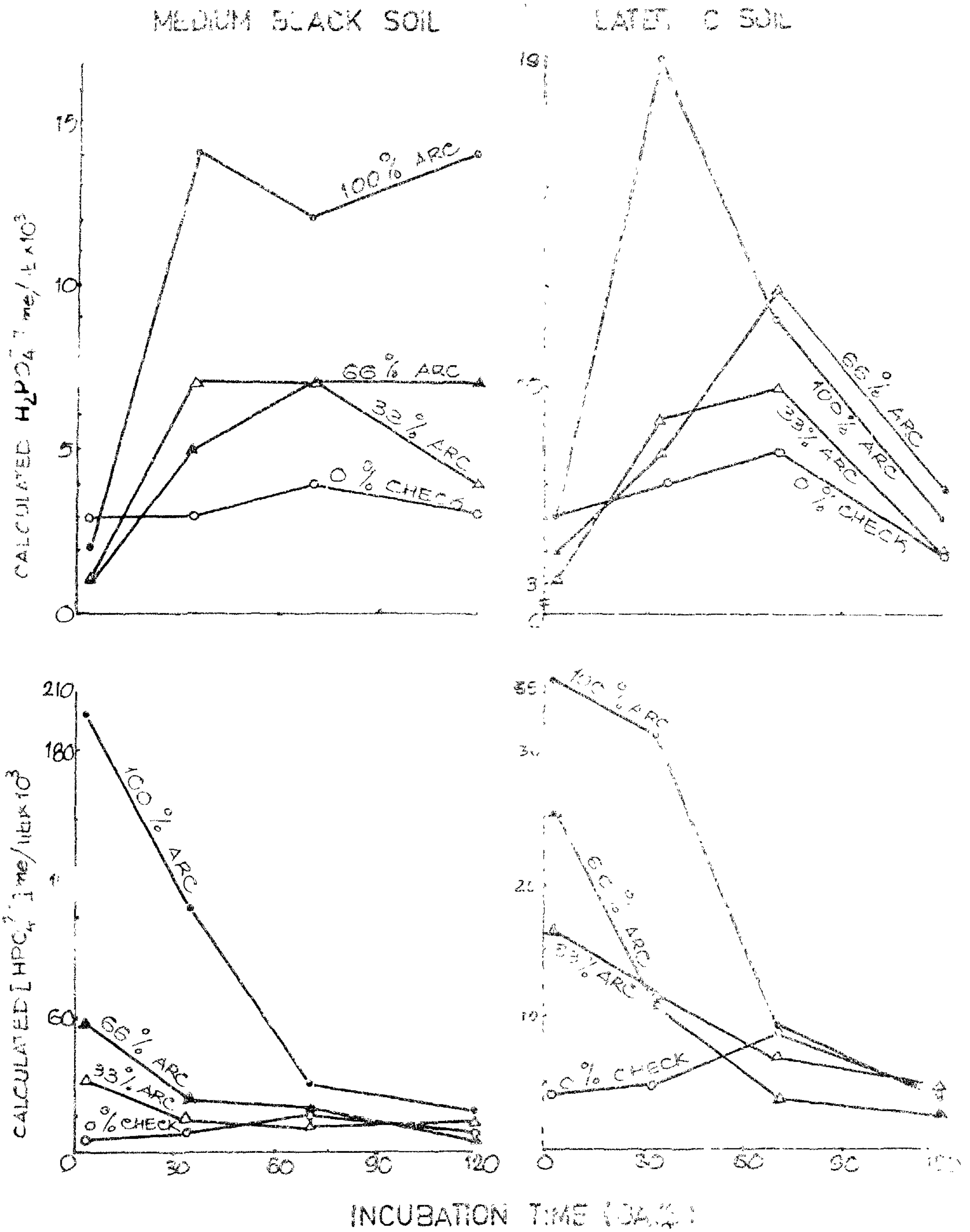


Fig 18 : Changes in calculated $H_2PO_4^-$ and HPO_4^{2-} concentrations in soil solution of ammoniated soils as influenced by incubation time.

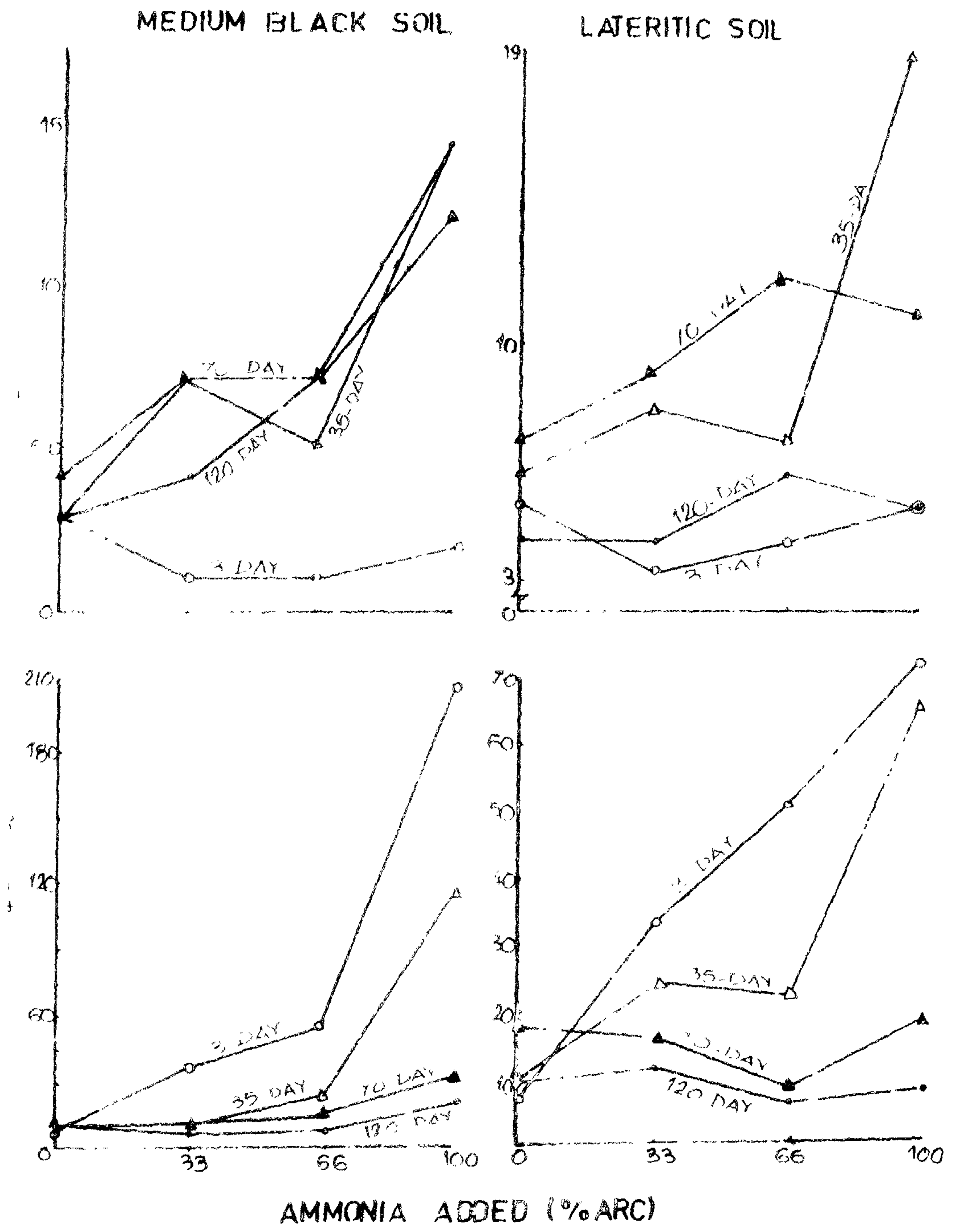


Fig 19 : Changes in calculated $H_2PO_4^-$ and HPO_4^{2-} concentrations in soil solution of incubated soils as influenced by added anhydrous ammonia.

lateritic soil with time showed more or less same trend, but the magnitude of P changes was smaller when compared with that in the case of medium black soil.

It is interesting to note that, as a result of ammoniation of the soils, by and large, total P measured in soil solution was increased. As a result of anhydrous NH_3 application in derno-podzolic soil, Iglorikov and Kulakov (1970) noticed higher contents of mobile P near the point of application.

4.5 Organic carbon content of soil solution :

A marked increase in soil pH following application of NH_3 in its retention zone is a common phenomena. Khengre(1976) noticed soil pH of 9.7 in the vicinity of ammonia injection point in vertisol. The soil solution pH rose from 7.4 to 8.9 when the same medium black soil (vertisol) was ammoniated equal to 100% AHC (Table 6). It is reported that solubility of soil organic matter increases with increase in soil pH (Schnitzer and Khan, 1972). Organic carbon content, in soil solution was measured and the data are reported in Table 21 and Fig. 20 and 21 . Increase in organic carbon in soil solution of both the soils studied was apparent. However, the ammount of organic carbon solubilized was small, probably dueto low organic matter content (medium black soil) or presence of most of the organic matter in clay-organic matter complexes (lateritic soil). The increased soluble organic carbons (probably organic anions) in soil solution may have provided complexing agents (ligands) which, probably were responsible for maintaining Fe and Mn in soil solution (Table 14).

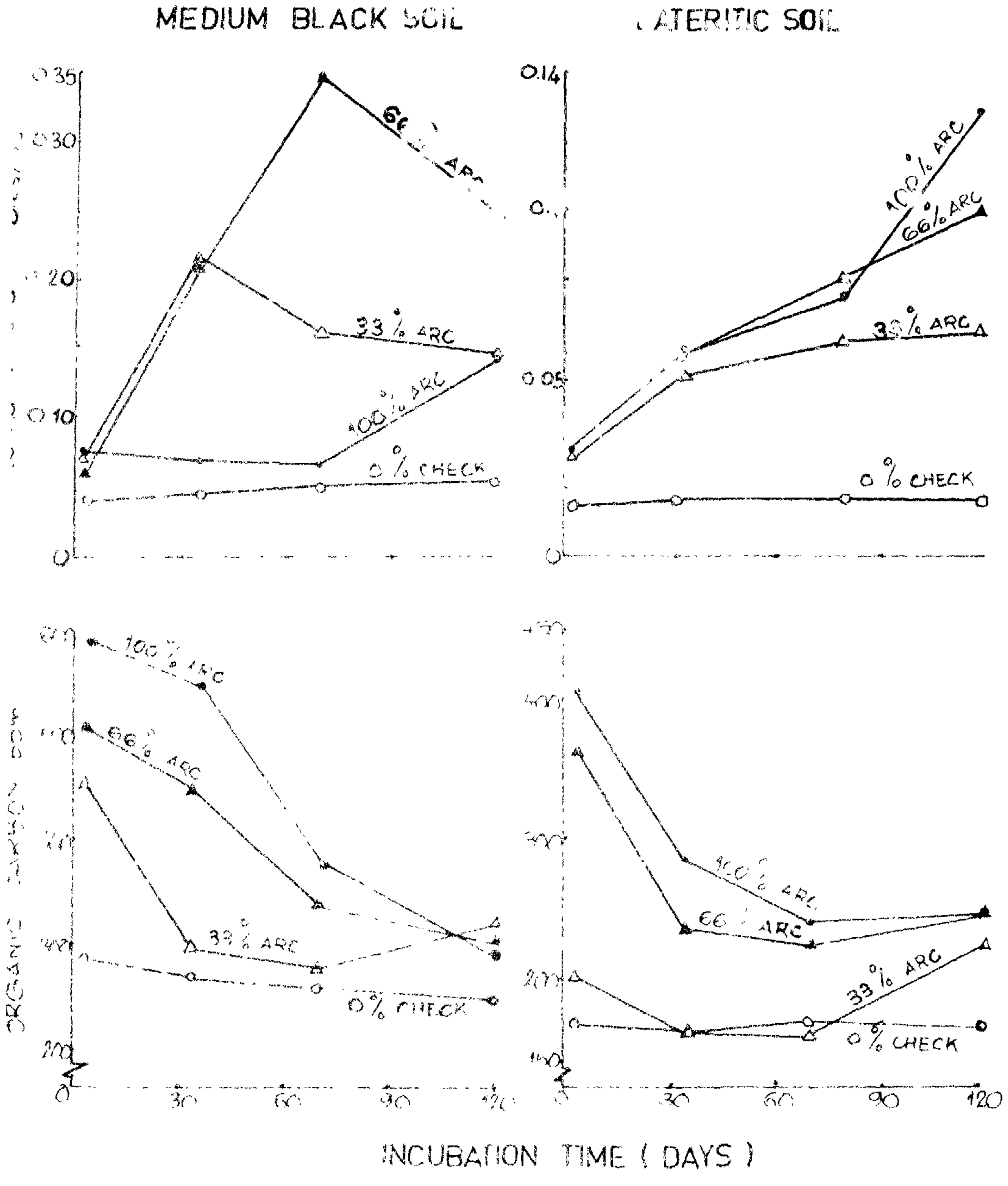

MEDIUM BLACK SOIL
LATERITIC SOIL
0.35
0.30
0.20
0.10
0
0.14
0.05
0
66% ARC
33% ARC
100% ARC
0% CHECK
100% ARC
66% ARC
33% ARC
0% CHECK
100% ARC
66% ARC
33% ARC
0% CHECK
100% ARC
66% ARC
33% ARC
0% CHECK
ORGANIC CARBON
200
400
300
200
150
0
30
60
90
120
0
30
60
90
120
INCUBATION TIME (DAYS)

Table 21 : Measured concentration of organic carbon in soil solutions of medium black and lateritic soils as influenced by added anhydrous NH_3 with time

NH_3 added (%AAC)	Organic carbon			
	Incubation time (days)			
	3	35	70	120
	ppm			
	medium black soil			
0 (check)	280	264	258	250
33	436	298	275	333
66	507	446	341	305
100	588	553	379	300
	lateritic soil			
0 (check)	168	161	171	170
33	206	168	152	226
66	263	235	226	250
100	406	287	242	250

4.6 Sum of cations, and anions and normality of soil solution:

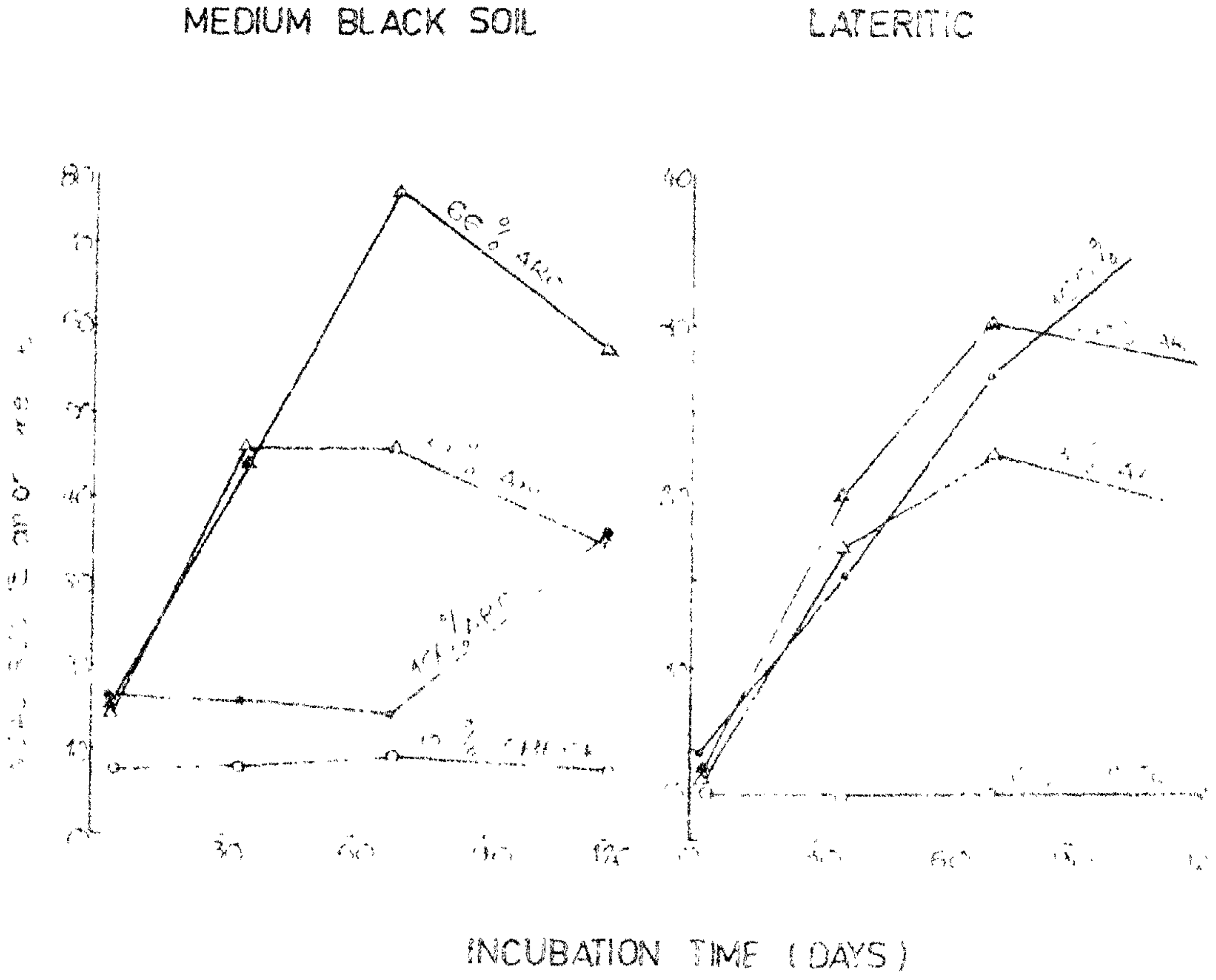
The changes in sum of cations (Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}+ NH_4^{+} were virtually similar to changes in measured concentrations of Ca and/or Mg in soil solution of the ammoniated soils (Fig 10 and 1 ~~6,7~~). This is because of predominance of Ca^{2+} and Mg^{2+} ions in the soil solution as compared with other cations in soil solution (Table 6,7,8). Figures 22 and 23 show that changes in sum of anions were markedly influenced by changes in NO_3^- in soil solution of the ammoniated soils with time .

Table 22 : Changes in measured total cations, total anions and ionic strength of soil solution of medium black soil as influenced by added anhydrous NH_3 and incubation time

NH_3 added (% AAC)	Incubation time (days)	Medium black soil			
		cations	anions	ionic strength	Normality
		me/liter	me/liter		N
0 (check)	3	10.35	12.96	0.015	0.010
	35	10.47	13.11	0.017	0.011
	70	11.72	14.42	0.019	0.012
	120	12.00	14.62	0.019	0.012
33	3	21.55	19.19	0.027	0.022
	35	51.93	51.30	0.073	0.052
	70	43.62	49.88	0.057	0.044
	120	36.12	38.37	0.053	0.036
66	3	25.82	20.15	0.030	0.026
	35	50.95	48.30	0.073	0.051
	70	82.28	80.98	0.120	0.082
	120	60.22	51.11	0.087	0.060
100	3	26.98	21.81	0.031	0.027
	35	22.70	20.56	0.02[illegible]	0.023
	70	22.49	18.08	0.034	0.023
	120	37.74	39.47	0.054	0.038

Table 23 : Changes in measured total cations, total anions and ionic strength of soil solution of lateritic soil as influenced by added anhydrous NH_3 and incubation time

NH_3 added ([illegible])	Incubation time (days)	Lateritic soil			
		cations	anions	ionic strength	normality
		me/liter			N
0 (check)	3	4.50	4.74	0.006	0.005
	35	4.55	5.15	0.006	0.005
	70	4.77	5.88	0.007	0.005
	120	4.76	5.76	0.007	0.005
33	3	10.41	6.68	0.011	0.011
	35	12.63	18.98	0.020	0.012
	70	15.80	24.59	0.026	0.016
	120	18.11	21.79	0.026	0.018
66	3	12.55	7.32	0.014	0.013
	35	17.62	21.46	0.025	0.018
	70	22.98	32.97	0.035	0.023
	120	27.54	31.37	0.039	0.028
100	3	14.30	8.99	0.015	0.014
	35	19.50	17.09	0.024	0.019
	70	23.11	29.13	0.0[illegible]	0.023
	120	36.63	41.46	0.052	0.037


MEDIUM BLACK SOIL
LATERITIC
80
60
40
10
0
30
60
90
120
66% ARC
INCUBATION TIME (DAYS)

22: [illegible]

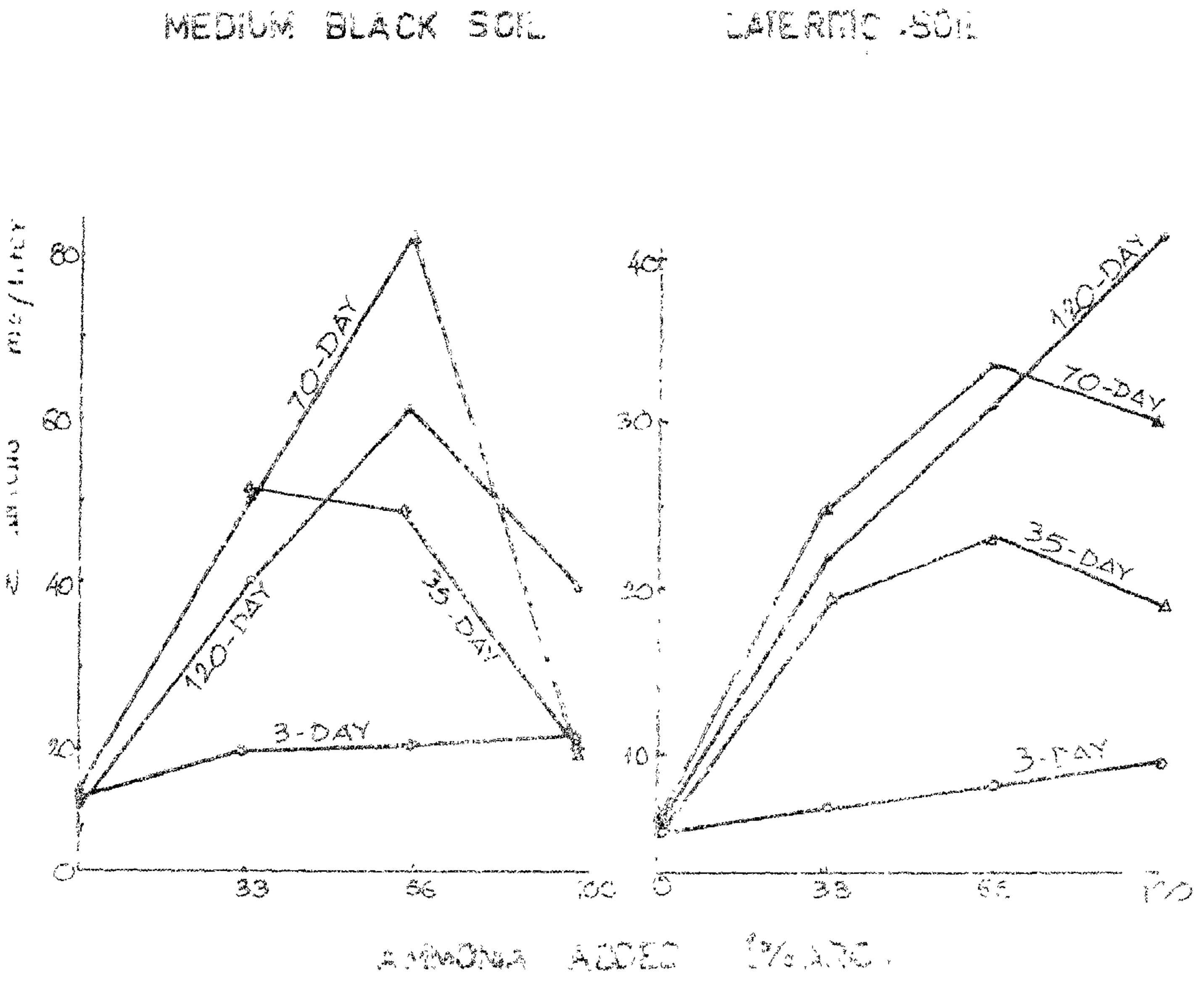


Fig. 23 Changes in total anion concentration in the soil solution of the incubated soils as influenced by added aqueous ammonia.

Normality of soil solution of the check soils varied from 0.0045 (lateritic soil) to 0.0103 (medium black soil). It increased with increasing levels of ammoni tion and in general increased with increasing incubation time. The highest normality of soil solution recorded, was 0.0823 when medium black soil was ammoniated equal to 66% AHC and incubated for 70-days. The highest normality in the case of lateritic soil was 0.0366 when it was ammoniated equal to 100% AHC and incubated for 120 days.

4.9 Calculated ionic concentration and ionic activity in soil solution :

The significance of calculated ionic activities in equilibrium soil solution is now sufficiently well documented (Pearson, 1971; Khasawneh, 1971). The principles of ion-pair formation and ionic activities in mixed dilute electreolyte solutions (anlogous to equilibrium soil solutions), are being used by soil chemists to elucidate soil chemical reactions such as, cation-exchange, clay mineral stability, etc. The measured ionic concentration in displaced soil solution can be corrected to ionic activities, by following the procedure suggested by Adams (1971). This procedure distributes soil solution electrolytes at equilibrium amoung their various ionic species, by using a score of related equations for ion-activity coefficients, ion-pair dissociation, weak-acid and weak-base dissociation and hydrolysis. Adams (1971) has advocated a method of successive approximations to be continued until all ionic concentrations remained unchanged with successive calculations. Numerous iterations ranging from 31 to 80 were required by him for getting the final estimates of ionic and ion-pair concentrations and ionic activities. Because of numerous equations to solve, and unavailability of computer facilities, ionic concentrations and ionic activities in soil solution were calculated with the help of desk-calculator upto first approximation only and the pertinent data are reported in the appropriate Table 7 through 19 .

The calculated (or so-called actual) concentrations of Ca^{2+}, Mg^{2+}, NH_4^+, HCO_3^- and SO_4^{2-} were always less than that measured. As propensity of SO_4^{2-} for ion-pairing, especially with divalent cation like Ca^{2+} and Mg^{2+}, its calculated ionic concentrations were significantly reduced. In most of the cases, their values were negative. This may be due to two reasons :

i) The calculations were carried out upto first approximation only. That is, more iterations were necessary.

ii) Some measuremental errors in the analytical procedure.

By and large, effects of added NH_3 and incubation time on calculated ionic concentrations were similar to those on measured ionic concentrations.

Table 25 : Calculate concentration of ion pairs ($CaSO_4^o$, $MgSO_4^o$, $NH_4SO_4^-$, $CaHCO_3^+$, $MgHCO_3^+$) in soil solution of lateritic soil as influenced by added anhydrous NH_3 with time

NH_3 added (% MRC)	Incubation time (days)	Lateritic soil				
		Ion-pairs				
		$CaSO_4^o$	$MgSO_4^o$	$NH_4SO_4^-$	$CaHCO_3^+$	$MgHCO_3^+$
		mmole/liter				
0 (check)	3	0.03	0.02	0.01	0.01	0.002
	35	0.04	0.02	0.01	0.01	0.002
	70	0.06	0.03	0.01	0.01	0.002
	120	0.05	0.02	0.01	0.01	0.002
33	3	0.08	0.05	0.04	0.01	0.009
	35	0.13	0.05	0.02	0.02	0.007
	70	0.11	0.05	0.01	0.01	0.006
	120	0.12	0.05	0.01	0.02	0.009
66	3	0.08	0.04	0.05	0.02	0.009
	35	0.17	0.07	0.04	0.03	0.010
	70	0.11	0.04	0.01	0.02	0.007
	120	0.14	0.06	0.02	0.03	0.011
100	3	0.09	0.06	0.09	0.02	0.013
	35	0.24	0.11	0.08	0.03	0.012
	70	0.17	0.06	0.03	0.02	0.005
	120	0.24	0.12	0.03	0.04	0.016

Table 26 : Calculated concentration of ion pairs ($CaSO_4^o$, $MgSO_4^o$, $NH_4SO_4^-$, $CaHCO_3^+$, $MgHCO_3^+$) in soil solution of medium black soil as influenced by added anhydrous NH_3 with time

NH_3 added (% ANC)	Incubation time (days)	Medium black soil				
		Ion-pairs				
		$CaSO_4^o$	$MgSO_4^o$	$NH_4SO_4^-$	$CaHCO_3^+$	$MgHCO_3^+$
		mmole/liter				
0 (check)	3	0.15	0.05	0.01	0.02	0.01
	35	0.22	0.07	0.01	0.03	0.01
	70	0.25	0.09	0.01	0.04	0.01
	120	0.25	0.10	0.01	0.03	0.01
33	3	0.23	0.08	0.04	0.07	0.02
	35	0.72	0.22	0.02	0.05	0.01
	70	0.60	0.13	0.01	0.04	0.01
	120	0.49	0.12	0.02	0.09	0.02
66	3	0.37	0.13	0.11	0.08	0.02
	35	1.04	0.26	0.04	0.06	0.01
	70	0.88	0.22	0.02	0.07	0.02
	120	0.76	0.17	0.03	0.15	0.03
100	3	0.42	0.07	0.17	0.09	0.01
	35	0.59	0.10	0.31	0.04	0.01
	70	0.39	0.12	0.21	0.02	0.01
	120	1.13	0.40	0.13	0.07	0.02

Ionic activities of soil solutions of ammoniated soils at all the 4 levels and at all incubations studied were always considerably less than the corresponding measured ionic concentrations. These differences were less apparent in the case of monovalent ions such as K^+, Na^+, NO_3^- and Cl^- but markedly noticed in the case of divalent cations studied such as Ca^{2+}, Mg^{2+} and SO_4^{2-}. These results, were expected and can be explained on the basis of ionic concentration-activity relationship. Because of increase in ionic strength, of soil solutions due to ammoniation of soil (Table 25) and the chemical transformations of added NH_3 during incubation, ionic activity of soil solutions may not have increased proportionately though there were increases in measured ionic concentrations. The changes in activities of soil-solution ions of ammoniated soils were more or less similar but of much smaller magnitude as compared with those in measured ionic concentrations.

Chapter 5

SUMMARY

The objective of the present investigation was to study the composition of soil solution as influenced by added anhydrous ammonia with time. For this purpose, two surface soils medium black clay (vertisol, from MPKV, Central Farm, Rahuri) and lateritic clay loam (from ARS, Radhanagari, District Kolhapur) were ammoniated (Pepandick and Parr, 1965) equal to 0, 33, 66, and 100% ammonia retention capacity (ARC) to simulate concentration gradient in the NH_3-retention zone following its application. The NH_3-treated soil samples were incubated at 27 ± 3 C for 1, 35, 70 and 120 days, and then soil solutions were obtained by Richards's pressure membrane method (1941). Measured ionic concentrations in soil solution were corrected to ionic activities using Adams method of successive approximations (1971). However, in the present study, ionic activities were calculated using first approximation only.

Soil solution pH markedly increased following addition of NH_3, but decreased with incubation time mainly due to acidifying effect of nitrification of NH_3. The measured soil-solution cations Ca^{2+}, Mg^{2+}, Na^+ and K^+ in the medium black soil showed by and large, increase with increasing levels of ammoniation, upto 70-day incubation time, but tended to decrease thereafter, while in the case of lateritic soil continuous increase in concentrations of these cations due to ammoniation was observed during incubation time. These results are explained on the basis of cation-exchange, precipitation and dissolution and nitrification reactions.

Measured NH_4^+ concentration in soil solution of the ammoniated soils equal to 33 and 55 per cent decreased rapidly due to oxidation of NH_3 to NO_3^-, whereas it decreased slowly in the case of ammoniated soils equal to 100 % AAC. The changes in soil-solution Fe and Mn of ammoniated soils appeared to be largely influenced by the changes in soil-solution pH.

As regards soil-solution anions namely Cl^-, SO_4^{2-} no definite effect of soil ammoniation and incubation time on them was observed. There was considerable increase in NO_3^-

concentration in soil solution due to oxidation of NH_4^+ to NO_3^- in both the soils studied. Carbonate ions were noticed after 3-day incubation only in the case of ammoniated medium black soil. The measured HCO_3^- concentration in soil solution increased in the ammoniated soils after 3-day incubation but it decreased thereafter. In general, measured phosphates increased in soil solution of the ammoniated soils. Ammoniation of the soil studied, probably solubilized organic matter resulting in more organic carbon in the soil solutions.

Normality of the soil solution increased due to the ammoniation of soils and the highest normalities recorded were 0.082 N and 0.037 N for the medium black soil (65 % AAC) and for the lateritic soil (100 % AAC) respectively. Electrical conductivity and ionic strength of the soil solution also showed a marked increase as a result of addition of ammonia to the soils.

The calculated ionic concentrations of the ammoniated soils were always less than that measured largely due to the assumption that soil solution was a mixed electrolyte solution containing ion-pairs. As expected, the activities of soil-solution ions were distinctly less on all occassions as compared with measured ion concentrations in soil solution due to addition of ammonia to the soils. Although trends in the changes in ionic activities in soil solution of ammoniated soils were apparently comparable with those in measured ionic concentrations, the magnitude of these changes were relatively smaller in the former.

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