A STUDY OF THE EFFECT OF SALTS ON THE SOLUBILITY AND MOBILIZATION OF SOIL NUTRIENTS

EBTEHAR ABDUL KAREEM AHMAD, B.Sc.

A thesis presented to the University of Glasgow for the degree of M.Sc. in the Faculty of Science.

Agricultural Chemistry Section
Chemistry Department
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TO MY HUSBAND AND FAMILY TO WHOM I OWE MUCH......

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SUMMARY

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SUMMARY

Many of the soils of Iraq have salinity problems. The causes of soil salinity were considered. These are principally evapontranspiration of irrigation water containing large amounts of salts, and a rising ground water table through saline soil profiles. A secondary cause is the effect of large amounts of fertilizer.

The work reported in this thesis is concerned with an examination of saline soils. The investigation set out to measure the concentrations of the soluble ions and their relationship with each other. Thus ions studied are those involved in saline soils and which affect plant growth.

The soil samples used in this work were taken from the banks of the Forth estuary, which is periodically flooded by estuarine water. This is one of the few situations where saline soils are found in temperate climates. The soils were analysed, as was the plant cover and standing water.

It was found that Na and Cl were the dominant ions in these soils, while Mg and SO_4 were present in lesser amounts. Similar amounts of Ca were found in both the flooded (gleyed and muck soil) and non flooded soils (brown earth soil). In the brown earth, Ca and Mg were the predominate cations with lesser amounts of Na and K.

The analysis of standing water indicated that the predominate

ions were Cl and Na, and the order of cation concentrations were :-

$$Na > Mg > Ca > K$$

The cation exchange capacity of the gleyed soil was higher than muck and brown earth soils.

Physical analysis showed that these soils had a very fine texture and had a very low permeability under saturation conditions (less than 1.4 x 10^{-4} cm/sec).

In experiments carried out to measure the effects of different salts (NaCl, Na_2SO_4, KCl, K_2SO_4, $MgCl_2$, $MgSO_4$, $CaCl_2$, $CaSO_4$) on the solubility of soil cations two concentrations were used - low concentration (0, 2, 5 , 10 meq/l and high concentration (20, 40, 60, 80 meq/l).

It was found that with a few exceptions at dilute concentrations the order of displacement of cations followed the lyotropic series :-

$$Ca > Mg > K > Na$$

while with anions the order was $SO_4 > Cl$.

However at high concentrations conflicing results were obtained due to interferences,(such as insolubility, ion pairs etc.) which changed the order of efficiency of displacement of the cations.

Since phosphate is an essential plant nutrient, the effect of salts on its solubility was studied. Some experiments were carried out on the native phosphate in the soil.

It was clearly shown that the type of salt had more effect on decreasing the native phosphate in gleyed soil than in brown soil, and also with the same soil the salt had a greater effect on PO_4 with top soil than with sub soil.

In most cases the addition of Cl reduced the solubility of native phosphate more than SO_4. The relative effect of different cations on the solubility of phosphate was not in the same order as the lyotropic series. The effects differ with the type of salt added and with soil depth.

In other experiments phosphate solution was added to the soil in different amounts.

In general, the presence of salts reduced the solubility of phosphate. Sulphate had a less marked effect on the solubility of phosphate than chloride, while in the case of salts with the same anion, the decrease in the solubility of phosphate was in the order :-

$$\mathrm{Na} > \mathrm{K} > \mathrm{Mg} > \mathrm{Ca}$$

This can be accounted for by interactions between salt solution and soil. This work suggested that soil salinity restricts the amount of soluble phosphate in soil solution. This could explain why in saline soils the amount of phosphate available to the plant might be lower than that available in a non-saline soil.

The effect of salt on calcareous soil was also studied. To simulate calcareous soils, powdered calcium carbonate was added to soil samples. The solubility of cations when salt solutions were applied was found to be lower in the treated soil than in the controls except in the case of calcium.

The effect of salt on the dissociation of Ca from calcium carbonate was found to be greater in the case of SO_4 than Cl, while with the same anion the difference between cations can be explained by a valency effect.

The effect of NaCl and $MgCl_2$ for individual and mixed samples of these salts showed a marked increase in the solubility of Ca in the case of the mixture, compared with the individual salts.

This suggested that the leaching of calcareous soil is less effective in removing salts from the soil than the leaching of a non-calcareous soil.

The higher mobility of calcium carbonate under saline conditions may give rise to problems if it is reprecipitated, e.g. problems such as the blockage of drains and conduits where an excess of non saline irrigation water is used to remove the salt from the soil profile and also the soil structure may be damaged. To remedy this may be very expensive. Alternative solutions include addition of calcium sulphate to the soil or to the irrigation water and the growing of crops which can tolerate the salinity.

The addition of monovalent salts was found to increase conductivity more than divalent, thus indicating that monovalent salts have a more important effect on soil salinity. Thus the total concentration of the salts present is not proportional to the conductivity.

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LIST OF ABBREVIATIONS

T.S.S.	Total soluble salt
meq/l	milliequivalent per litre
E.C.	Electrical conductivity
gm.	gram
S.P.	Water saturation percentage
mol P/l	mol phorphorus per litre
min.	minute
temp.	temperature
S.A.P.	Sodium adsorption percentage
S.S.P.	Soluble sodium percentage
E.S.P.	Exchangeable sodium percentage
C.E.C.	Cation exchange capacity
p.p.m.	Parts per million
n.d.	Not determined.

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The addition of monovalent salts was found to increase conductivity more than divalent, thus indicating that monovalent salts have a more important effect on soil salinity. Thus the total concentration of the salts present is not proportional to the conductivity.

CHAPTER ONE

INTRODUCTION

Irrigation has been used successfully for a long time in Egypt and China and their lands still produce good crop yields.

In Mesopotamia however irrigation failures occurred where an early great civilization developed in the valley formed by the Tigris and Euphrates rivers. This civilization has collapsed for a variety of reasons, a decrease in the agricultural productivity occurred and Mesopotamia suffered from waterlogging and salinity problems.

Methods of irrigation are considered to be one of the most important factors which affect salt distribution on agricultural land.

Bernstein and Fireman (1957) described the distribution of salts resulting from furrow irrigation. Goldberg et al (1971) gave partial results on moisture depletion and salt distribution patterns using springlers for irrigating a vineyard.

Soil salinity occurs in regions of arid and semi arid climates mainly by precipitation of salts which can be recognised by the white crust formed on the surface of some Iraqi soils. These soils correspond to Hilgard's (1906), "white alkali soils", and to the "Solonchak" of the Russian soil scientists

(Russell 1961).

Saline and alkali soils had been studied by many workers before the turn of the century,(Hayward and Wadleigh 1949).

The terminology and classification proposed by Magistad (1945) and the U.S. Salinity Laboratory (1947) for saline and alkali soils are :-

1 Saline ~~Alkali~~ soil
2 Non saline - alkali soil
3 Saline - alkali soil
4 Alkaline ~~Saline~~ soil

In brief, the first three soils contain sufficient exchangeable sodium to interfere with the growth of most plants. In addition, alkali soil may or may not contain sufficient quantities of soluble salts. Non saline soil does not contain sufficient quantities of soluble salts. The exchangeable sodium percentage of this class (non saline - alkali soil) is greater than 15, the electrical conductivity of saturation extract is less than 4 mmohs/cm at 25°C and the pH of the saturation soil usually 8.5 - 10.0.

In the saline-alkali soil the exchangeable sodium percentage is greater than 15, the electrical conductivity is more than 4 mmhos/cm and the pH is usually less than 8.5.

Saline soil refers to a non alkali soil containing soluble salts in such quantities that they interfere with the growth of most plants. Its conductivity is greater than 4 mmhos/cm, the exchangeable sodium percentage is less than 15 and the pH is less than 8.5. The cations involved in saline soils are usually Ca , Mg , K and Na , while the chief anions are Cl and SO_4 . Small amounts of nitrate and bicarbonate may occur but soluble carbonates are invariably absent (Hesse 1971).

The presence of salts however in soluble form produce high salinity which is shown by high conductivity. The solubility of salts are shown in Table (2.1) (Hodgman <u>et</u> <u>al</u> 1960).

The standards of evaluating soil salinity differ from country to country.

According to the U.S. system, saline soils of Iraq, for example, are grouped according to their content of total soluble salts into five classes, as shown in Table (1.5). This classification in Algeria is based on the soil chloride content, (Bonlaine 1956).

Salinization of soils may be increased by agricultural mismanagement. One of the important factors in this respect is the use of excess water in irrigation which leads to a rise in the ground water table. Under high potential evapotranspiration, salts accumulate on the soil surface and interfere with plant growth.

? is it not the absence of adequate drainage which is crucial as excess water is required to leach soluble salts from the soil

The use of high fertilizer dosage where the fertilizer has a high salt index may increase soil salinity,(Jackson 1962), which does occur with the Iraqi soils. This is especially true with phosphorus on mineral soils and potassium on organic soils.(Cook and Davis 1957).

Most of the Iraqi soils have suffered from salinity problems due to mismanagement of irrigation over the years. Consequently much of the land can be used for cropping only in alternate years. The productivity of such land is considered to be very low. Thus a systematic planned removal of salts is required from an irrigation scheme. A proper leaching, drainage and good management scheme should bring about a great improvement.

1.1 Classification of irrigation water quality

It was recommended (U.S. Salinity Laboratory staff, 1954 and Wilcox 1955) that irrigation water quality should be classified as follows :-

1 Total salinity
2 Sodium content
3 Boron content
4 Bicarbonate content

1 The most important criterion of irrigation water quality is probably the total salt concentration. Waters are divided

into four different classes on the basis of electrical conductivity measurements as :-

(i) Low salinity < 250 μmhos/cm (C_1)
(ii) Medium salinity 250 - 750 μmhos/cm (C_2)
(iii) High salinity 750 - 2250 μmhos/cm (C_3)
(iv) Very high salinity $>$2250 μmhos/cm (C_4)

2 Waters are divided into four classes with respect to the sodium hazard based on sodium adsorption ratio

$$\text{S.A.R.} = \frac{\text{Soluble sodium in meq/l}}{\sqrt{\dfrac{\text{Soluble (calcium + magnesium) in meq/l}}{2}}}$$

At an electrical conductivity value of 100 μmhos/cm at 25°C they are :-

(i) Low S.A.R. < 10 (S_1)
(ii) Medium S.A.R. 10 - 18 (S_2)
(iii) High S.A.R. 18 - 26 (S_3)
(iv) Very high S.A.R. > 26 (S_4)

These S.A.R. values are inversally proportional to the electrical conductivity values.

3 Boron has been considered as a very toxic element to plants at low concentration. The permissible levels for several classes of irrigation waters are tabulated in Table (1.1),(Scofield 1936).

4 The bicarbonate hazard is expressed in terms of the residual sodium carbonate - R.S.C. =

$$(CO_3^{=} + HCO_3^{-}) - (Ca^{2+} + Mg^{2+})$$ (Eaton 1950)

The bicarbonate tends to precipitate calcium and magnesium, so the relative proportion of sodium remaining in the water is increased and the sodium hazard is also increased.

1.2 The effect of salts on plant growth

Plant growth responses to salinity have been discussed (Hayward and Wadleigh 1949 ; Grillot 1956; Bernstein and Hayward 1958).

Salts affect plant growth by :-

1 Increasing the osmotic pressure of soil solution
2 Accumulation of certain ions in toxic concentrations in plant tissue
3 Altering the plant mineral nutrition

1 Growth reductions associated with increasing osmotic pressure of the root medium has been attributed to decreasing water entry or availability (Hayward and Spurr 1943 and 1944).

The valency and amount of salts present such as $NaCl$, Na_2SO_4, KCl, K_2SO_4, $MgCl_2$, $MgSO_4$, $CaCl_2$ and $CaSO_4$ control the osmotic pressure of soil solution which in turn affects the physiological availabilityof water (Eaton 1941 and Long 1943).

However, Bernstein (1961) indicates that water absorption capacity which is relatively unaffected by salinity and growth reduction associated with osmotic stress, is attributed to the build up of osmotic pressure of developing cells to meet the increasing osmotic pressure of the rooting medium.

2. Certain ions can depress plant growth and yield independent of osmotic effects. These specific ion effects

may be toxic(or beneficial)in nature. The toxic effect results in direct damage to the plants. Injury is usually associated with the accumulation of harmful concentrations of the toxic ions in the plant tissues.

3 Salinity may reduce plant growth because of its effect on plant nutrition. This effect however differs from species to species as plants vary widely in their nutrient requirements and in their ability to absorb specific nutrients. Hayward and Wadleigh (1949) reported that high concentrations of sulphate generally decrease the uptake of the calcium while promoting the uptake of sodium.

Plants however have different tolerances for soil salinity. This is shown in Table (1.6),(Allison 1964).

1.3 Soil reclamation

Saline soils continue to be a problem until the excess of both salts and exchangeable sodium are removed from the root zone, and a favourable physical condition in the soil is established.

The amount and kind of chemical amendment used for replacement of exchangeable sodium in soils depends upon the soil characteristics.

The chemical reaction of various amendments with soils are as follows :- (U.S. Salinity Laboratory Staff 1954)

1 In presence of carbonate :-

a) Gypsum :-

$$\text{clay}\Big]\begin{matrix}\text{Na}\\ \text{Na}\end{matrix} + CaSO_4 \longrightarrow \text{clay}\Big]\,\text{Ca} + Na_2SO_4$$

b) Sulphur :-

$$2S + 3O_2 \rightarrow 2SO_3 \quad \text{oxidation by micro-organism}$$

$$SO_3 + H_2O \rightleftharpoons H_2SO_4$$

$$H_2SO_4 + CaCO_3 \longrightarrow CaSO_4 + CO_2 + H_2O$$

or $$H_2SO_4 + 2CaCO_3 \longrightarrow CaSO_4 + Ca\,(HCO_3)_2$$

$$\text{clay}\Big]\begin{matrix}\text{Na}\\ \text{Na}\end{matrix} + CaSO_4 \longrightarrow \text{clay}\Big]\,\text{Ca} + Na_2SO_4$$

c) Iron sulphate :-

$$FeSO_4 + H_2O \rightleftharpoons H_2SO_4 + FeO$$

$$H_2SO_4 + CaCO_3 \rightleftharpoons CaSO_4 + CO_2 + H_2O$$

$$\text{clay}\Big]\begin{matrix}\text{Na}\\ \text{Na}\end{matrix} + CaSO_4 \rightleftharpoons \text{clay}\Big]\,\text{Ca} + Na_2SO_4$$

2 In the absence of carbonate :-

a) Gypsum :-

$$\left.\text{clay}\right]\begin{matrix}\text{Na}\\\text{Na}\end{matrix} + CaSO_4 \rightleftharpoons \left.\text{clay}\right]\text{Ca} + Na_2SO_4$$

b) Sulphur :-

$$2S + 3O_2 \rightleftharpoons 2SO_3 \qquad \text{oxidation}$$

$$SO_3 + H_2O \rightleftharpoons H_2SO_4$$

$$\left.\text{clay}\right]\begin{matrix}\text{Na}\\\text{Na}\end{matrix} + H_2SO_4 \rightleftharpoons \left.\text{clay}\right]\begin{matrix}\text{H}\\\text{H}\end{matrix} + Na_2SO_4$$

c) Iron sulphate :-

$$FeSO_4 + H_2O \rightleftharpoons H_2SO_4 + FeO$$

$$\left.\text{clay}\right]\begin{matrix}\text{Na}\\\text{Na}\end{matrix} + H_2SO_4 \rightleftharpoons \left.\text{clay}\right]\begin{matrix}\text{H}\\\text{H}\end{matrix} + Na_2SO_4$$

As mentioned previously the kind and amount of chemical amendment for soil reclamation is dependent on many factors such as, the soil pH and its alkali earth carbonate content as well as their reactions.

The addition of acid or acid formers have been used under alkali conditions to reduce the alkalinity.

Under acid conditions, or when the amendment makes the conditions excessively acid, limestone must be added to restrict the acidity such as in Hungary. These acid soils have special characteristics; they contain both excess exchangeable sodium and appreciable amounts of exchangeable hydrogen ions.

Two possibilities exist with regard to the reaction of limestone ($CaCO_3$) (Kelley and Brown 1934). These are as follows :-

1 $\text{clay}\Big]\begin{matrix}\text{Na}\\ \text{Na}\end{matrix} + CaCO_3 \rightleftharpoons \text{clay}\ \ Ca + Na_2CO_3$

2 $\text{clay}\Big]\begin{matrix}\text{Na}\\ \text{Na}\end{matrix} + HOH \rightleftharpoons \text{clay}\Big]\begin{matrix}\text{H}\\ \text{H}\end{matrix} + 2NaOH$

an excess of exchangeable hydrogen.

$$\text{clay}\Big]\begin{matrix}\text{H}\\ \text{H}\end{matrix} + CaCO_3 \rightleftharpoons \text{clay}\Big]\,Ca + CO_2 + H_2O$$

Generally Na_2CO_3 was not still in the soil as a salt but as $NaHCO_3$, CO_2 and OH .

The effect of lime on different soils is related to the effect of the solubility of $CaCO_3$ which is controlled by the pH value (Sigmond 1938), as follows :-

pH value of saturated $CaCO_3$		Solubility of $CaCO_3$ in meq/l
6.21	↑	19.3
6.5	$CaCO_3$ was more	14.4
7.12	effective in reclamation	7.1
7.85	↓ ↑	2.7
8.6	$CaCO_3$ was less	1.1
9.2	effective in reclamation	0.82
10.12	↓	0.3

1.4 Physical properties of soil

Physical properties of the soil depend on the soil structure. It was concluded that the soil structure is the arrangement of the soil particles and the pore space between them. (Russell 1971).

The organic fraction has a marked effect on the physical and chemical properties of the soil. Its effect is equally desirable on heavy and on light soil. Thus the aggregates are formed from fine textured soils containing high percentages of silt and clay.

Salts affect soil structure by their effects on flocculation and dispersion of soil particles. These two phenomena depend almost exclusively on the concentration and valency of these salts. The thresholds for flocculation fall in the ranges:- (Van Olphen 1963)

25 - 150	mmole/l	monovalent ions
0.50 - 2.0	"	divalent ions
0.01 - 0.1	"	trivalent ions

When the soil particles are dispersed the structure is damaged and the soil becomes unfavourable for the entry and movement of water (permeability).

The tillage of such soil becomes very difficult due to the alteration in soil consistency (Baver 1956).

1.5 Purpose of this study

This study was carried out in order to evaluate the effect of salts on the solubility of ions in the soil.

The soils used in this study were taken from Higgins Neuck on the south bank of the Forth estuary at Kincardine Road bridge. The Forth area was selected in this study because of its soil properties, which were considered to be more or less saline. The Forth soils are flooded by estuarine water.

Saline soils are not usually found in humid regions except around estuaries when the land has been flooded by estuarine waters or on other low lying land near the sea.

The Higgins Neuck soils do perhaps resemble one type of Iraqi soil (Hydomorphic Soil) (Buringh 1960, Buringh and Kadry 1956) which is either waterlogged or has a high ground water table and is characterised by a grey colour or iron mottled stains. This is found in combination with other soils in the marsh regions in the south of Iraq. The physiological and climatological properties of Iraqi soils are shown in the map, Fig (I). Most soils in mid and southern Iraq are saline, as shown in the map (Fig. II) and two types are common, Shuria (the dominant salts are NaCl and Na_2SO_4), and Subakh (the dominant salts are $CaCl_2$ and $MgCl_2$) (Al-Nakshabandi et al 1971).

In addition most Iraqi soils have a high amount of gypsum as shown in the map (Fig. III).

Soluble salt levels are usually reduced by dissolution and transportation by downward movement of water through the soil (leaching). Thus the soluble salt content of irrigation water is an important factor in the concept of soil improvement.

The quantity and quality of soluble salts in Iraqi rivers (Tigris, Euphrates, Shatt Al-ARAB and Diyala) have been investigated (Hanna et al 1970), as shown in Tables (1.2), (1.3) and (1.4). Samples were taken from 25 places as shown in the map (Fig. IV). It can be concluded from these Tables that high concentrations of sodium ions increase the ability of water to dissolve more calcium and magnesium as carbonate which increases the temporary hardness (CO_3 and HCO_3 expressed as $CaCO_3$) and total hardness (Ca + Mg expressed as $CaCO_3$).

By irrigation with hard water the concentration of calcium and magnesium carbonate will be increased in the soil, due to the evapotranspiration. This will increase the alkalinity of the soil and decrease the ability of water to penetrate through the soil (impermeable) due to clogging of the soil pores by $CaCO_3$ and $MgCO_3$.

CHAPTER TWO:

The experimental work was carried out to investigate the characteristics of the soil samples, which were used in this study.

CHAPTER THREE:

This study was undertaken to increase the understanding of the solubility of essential ions for plant growth in saline soils such as phosphate. The dependence of some of the results on the concentration of salt added could be explained by the Donnan equilibrium theory.

CHAPTER FOUR:

The effect of salts on calcareous soil was studied. To simulate calcareous soils, powdered $CaCO_3$ was added to soil samples. The higher mobility of $CaCO_3$ under saline conditions may give rise to problems if it is reprecipitated.

CHAPTER FIVE:

Experiments were performed on the solubility of native cations in the soil by displacement by added salts. This study was undertaken to find out the relationship between the degree of ion displacement and the concentrations of added salt, in addition to studying the difference in the influence of univalent and divalent ions over two concentration ranges (low and high concentration).

The displacement of different cations from the soil should show the importance of considering the interactions which occur in the soil when choosing the composition and level of fertilizer for a particular soil.

Appendix 1

Conductivity measurements were made to estimate qualitatively the fraction of salt ionized. The addition of monovalent and divalent salt to increase the conductivity and to find out which one has the most important affect on soil salinity was also included.

Table (1.1)

Permissible limits of Boron for several classes of irrigation water in ppm (Scofield 1936)

Boron class	For irrigation of		
	Sensitive crops	Semi-tolerant crops	Tolerant crops
1	< 0.33	< 0.67	< 1.00
2	0.33 - 0.67	0.67 - 1.33	1.00 - 2.00
3	0.67 - 1.00	1.33 - 2.00	2.00 - 3.00
4	1.00 - 1.25	2.00 - 2.5	3.00 - 3.75
5	> 1.25	> 2.5	> 3.75

Table (1.2)

Concentrations of cations and anions in the Tigris River (Hanna *et al* 1970)

	meq/l									µmhos/cm	p.p.m.					
	Na	K	Ca	Mg	Cl	SO_4	HCO_3	CO_3	S.A.R.	EC	P	N	K	Permanent hardness	Temporary hardness	Total hardness
															(CO_3 HCO_3 expressed as $CaCO_3$)	(By EDTA expressed as $CaCO_3$)
Mosul	0.5	0.1	2.7	1.8	0.7	1.4	2.9	0.3	0.3	404	< 0.1	0.3	2.3	65	160	225
Shirgate	0.5	0.1	2.7	1.6	0.8	1.2	2.9	0.3	0.3	391	< 0.1	0.8	2.3	55	160	215
Fatha	0.6	0.1	2.6	1.7	0.8	1.1	2.9	0.2	0.4	373	< 0.1	0.8	2.1	60	155	215
Samarria	0.5	0.1	2.4	1.6	0.8	1.0	2.9	0.3	0.4	379	< 0.1	1.0	2.3	40	160	200
Baghdad	1.4	0.1	2.6	2.2	1.5	1.6	2.6	0.3	0.9	507	< 0.1	0.3	2.6	95	145	240
Kut	1.3	0.1	2.8	2.3	1.4	1.6	2.7	0.3	0.8	537	< 0.1	0.2	2.5	105	150	255
Amara	2.0	0.1	3.4	2.1	2.1	2.4	2.7	0.3	1.2	650	< 0.1	0.4	2.5	125	150	275
Qurna	2.9	0.1	3.8	3.2	3.0	3.1	3.3	0.4	1.6	880	0.1	0.4	3.5	165	185	350

Table (1.3)

Concentration of cations and anions in Euphrates River (Hanna et al 1970)

	meq/l									µmhos/cm	p.p.m.					
	Na	K	Ca	Mg	Cl	SO_4	HCO_3	CO_3	S.A.R.	EC	P	N	K	Permanent hardness	Temporary hardness	Total hardness
															(CO_3 HCO_3 expressed as $CaCO_3$)	(By EDTA expressed as $CaCO_3$)
Al-Kaim	2.0	0.1	2.8	2.3	1.8	2.8	2.8	0.3	1.3	575	0.1	0.8	3.0	100	155	255
Hakalniy	1.7	0.1	3.0	2.3	2.0	1.7	2.8	0.4	1.0	608	0.1	0.4	3.5	105	160	265
Hit	1.7	0.1	2.8	2.3	1.9	1.8	2.7	0.3	1.1	600	0.1	1.0	3.4	105	150	255
Fallaja	1.6	0.1	2.7	2.1	1.9	1.7	2.7	0.3	1.0	568	<0.1	0.4	3.5	90	150	240
Musseyeb	1.6	0.1	2.7	2.1	1.8	1.6	2.4	0.3	1.0	559	<0.1	0.7	3.4	105	135	240
Kifl	1.9	0.1	3.0	3.4	2.1	1.8	2.9	0.3	1.1	618	<0.1	1.4	3.6	160	160	320
Samawa	4.3	0.1	3.3	3.5	4.9	3.0	2.9	0.3	2.3	984	0.1	0.8	4.5	180	160	340
Nasiriy	4.1	0.1	3.3	3.3	4.6	3.1	2.8	0.3	2.3	976	<0.1	0.7	4.2	175	155	330
Qurna	3.7	0.1	3.7	3.6	3.6	3.3	3.4	0.3	1.9	959	0.1	0.3	4.2	180	185	365
Hilla	1.6	0.1	2.7	2.2	1.2	1.5	2.6	0.3	1.0	578	<0.1	0.7	3.5	100	145	245
Diywainya	2.1	0.1	2.9	3.5	3.3	1.9	2.8	0.3	1.2	630	<0.1	0.8	3.6	165	155	320

Table (1.4)

Concentration of cations and anions in Shatt Al-Arab and Diyala Rivers. (Hanna *et al* 1970)

	meq/l									μmhos/cm	p.p.m.					
	Na	K	Ca	Mg	Cl	SO_4	HCO_3	CO_3	S.A.R.	EC	P	N	K	Permanent hardness	Temporary hardness	Total hardness
															(CO_3 HCO_3 expressed as $CaCO_3$)	(By EDTA expressed as $CaCO_3$)
Shatt Al-Arab																
Qrna	3.1	0.1	3.5	3.5	3.5	3.0	3.4	0.4	1.7	901	<0.1	0.4	4.2	160	190	350
Basra	5.4	0.2	3.4	4.0	3.8	3.7	3.0	0.3	2.8	1182	0.1	0.6	5.8	205	165	370
Fao	21.4	0.3	4.0	7.2	23.0	4.9	3.2	0.3	9.1	2803	0.1	2.2	13.0	385	175	560
Diyala																
Baquba	2.3	0.1	3.4	2.7	2.3	2.9	2.9	0.3	1.3	738	<0.1	0.4	2.8	145	160	305
Diyala-Bridge	3.8	0.1	4.1	3.9	3.6	3.6	3.0	0.3	1.9	1058	0.1	2.0	4.4	235	165	400

Table (1.5)

Soil salinity classes, Buringh (1960)

Soil class	Name	$E.c._{e.} \times 10^3$	T.S.S. %	Crops
0	Non saline	0 - 2	0.0 - 0.15	Salinity effect, is negligible
		2 - 4		Restricted yield of very sensitive crops
1	Slightly saline	4 - 8	0.15 -0.35	Restricted yield of many crops
2	Moderately saline	8 - 15	0.35 -0.65	Tolerant crops only
3	Strongly saline	>15	> 0.65	Very tolerant crops only

$E.c._{e.}$ = Electrical conductivity of saturation extract in millimhos/cm

T.S.S. = Total soluble salt content

Table (1.6)

Relative tolerance of crops to salinity arranged according to decreasing tolerance within groups, (Allison 1964)

Crop	Tolerant	Moderately Tolerant		Sensitive
Field	12-8 mmho/cm	8-4 mmho/cm		3-2 mmho/cm
	Barley	Rye	Broadbean	Field beans
	Sugar beet	Wheat	Corn	
	Rape	Oats	Rice	
	Cotton	Sorghum	Flax	
		Sorgo	Sunflower	
		Soybeans	Castorbean	
		Sesbania		
Pasture	8-5 mmho/cm	5-3 mmho/cm		3-2 mmho/cm
	Garden beets	Tomato	Yam	Radish
	Kale	Broccoli	Bell pepper	Celery
	Asparagus	Cabbage	Carrot	Green beans
	Spinach	Cauliflower	Onion	
		Lettuce	Peas	
		Sweet corn	Cantaloupe	
		Potatoes	Squash	
		Sweet potato	Cucumber	
Forage	12-6 mmho/cm	6-3 mmho/cm		3-2 mmho/cm
	Saltgrass	Sweetclover	Oats (hay)	White dutch clover
	Bermudagrass	Perennial ryegrass	Orchardgrass	Meadow foxtail
	Tall wheatgrass	Mountain brome	Blue grama	Alsike clover
	Rhodesgrass	Harding grass	Meadow fescue	Red clover
	Canada wildrye	Beardless wildrye	Reed canary	Ladino clover
	Western wheatgrass	Strawberry clover	Big trefoil	Burnet
	Tall fescue	Dallisgrass	Smooth brome	
	Barley (hay)	Sudangrass	Tall meadow oatgrass	
	Birdsfoot trefoil	Hubam clover	Milkvetch	
		Alfalfa	Sourclover	
		Rye (hay)		
		Wheat (hay)		
Fruit	8 mmho/cm	6-3 mmho/cm		3-1.5 mmho/cm
	Date palm	Pomegranate	Orange	Peach
		Fig	Grapefruit	Apricot
		Olive	Lemon	Boysenberries
		Grape	Apple	Blackberries
			Pear	Raspberries
			Plum	Avocado
			Prune	Strawberry
			Almond	

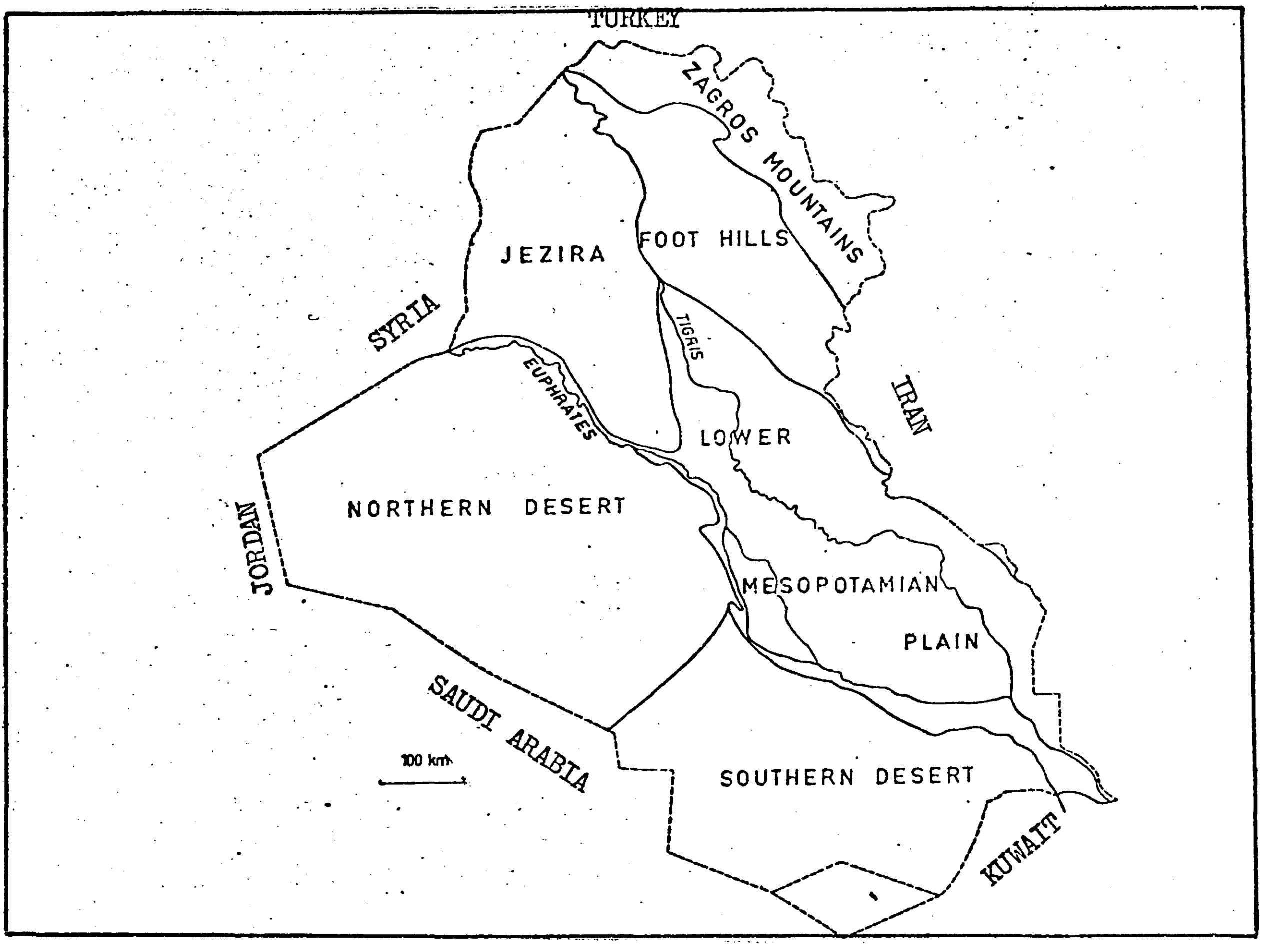


Fig. I Map of physiographic units of Iraq

Scale 1: 1 000 000

Buringh (1960)

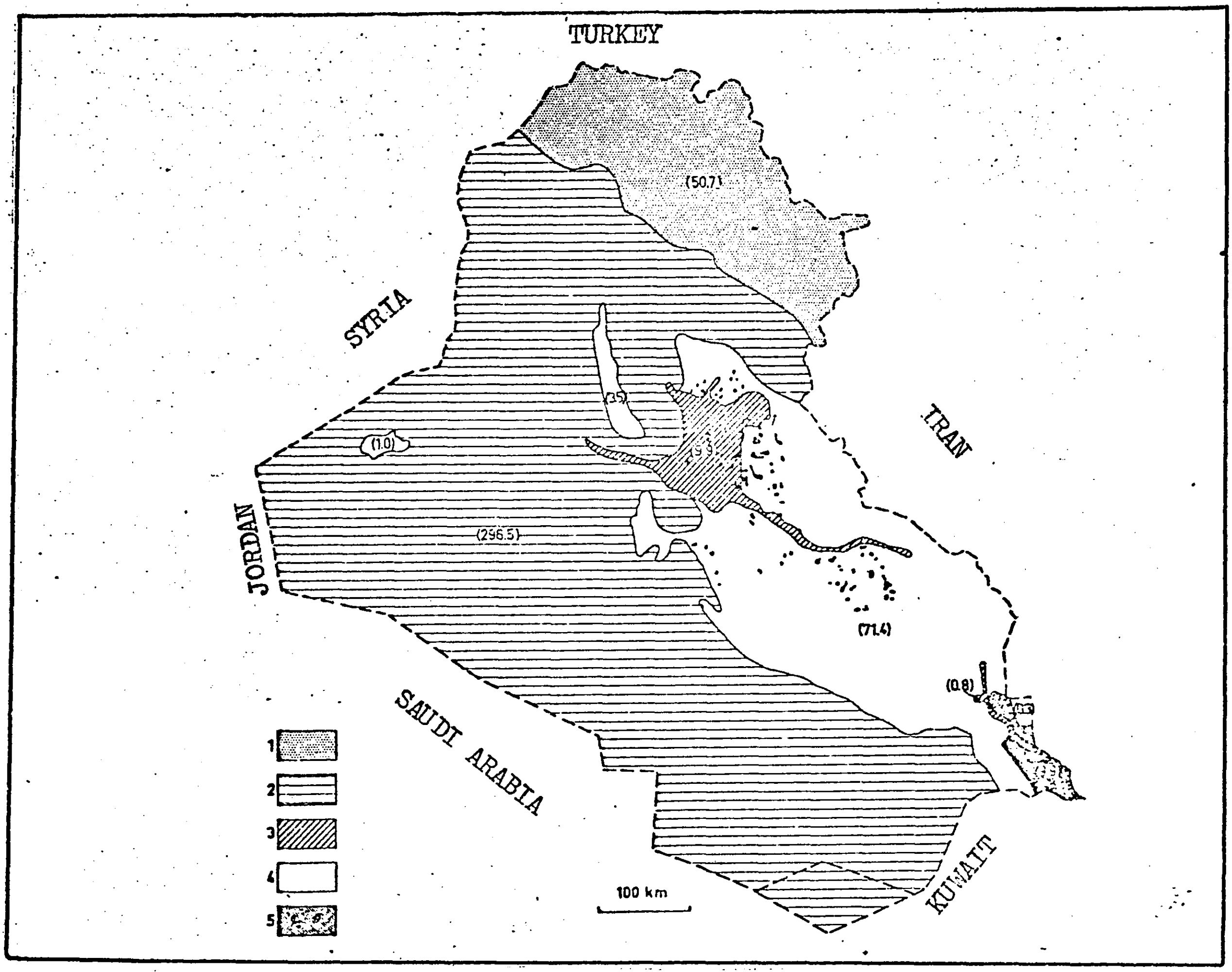


Fig. II Schematic map of salinization in soils of Iraq. 1. soils without salinization; 2. deserts and soils with some salinization locally; 3. soils with moderate salinization; 4. soils with severe salinization; 5. (and black dots) soils with salinization and solonization. (9.9)-area in 1000 km^2. Solodization processes have only been noticed in some small areas on Tigris terraces east of Samarra.

Scale 1: 1 000 000

Buringh (1960)

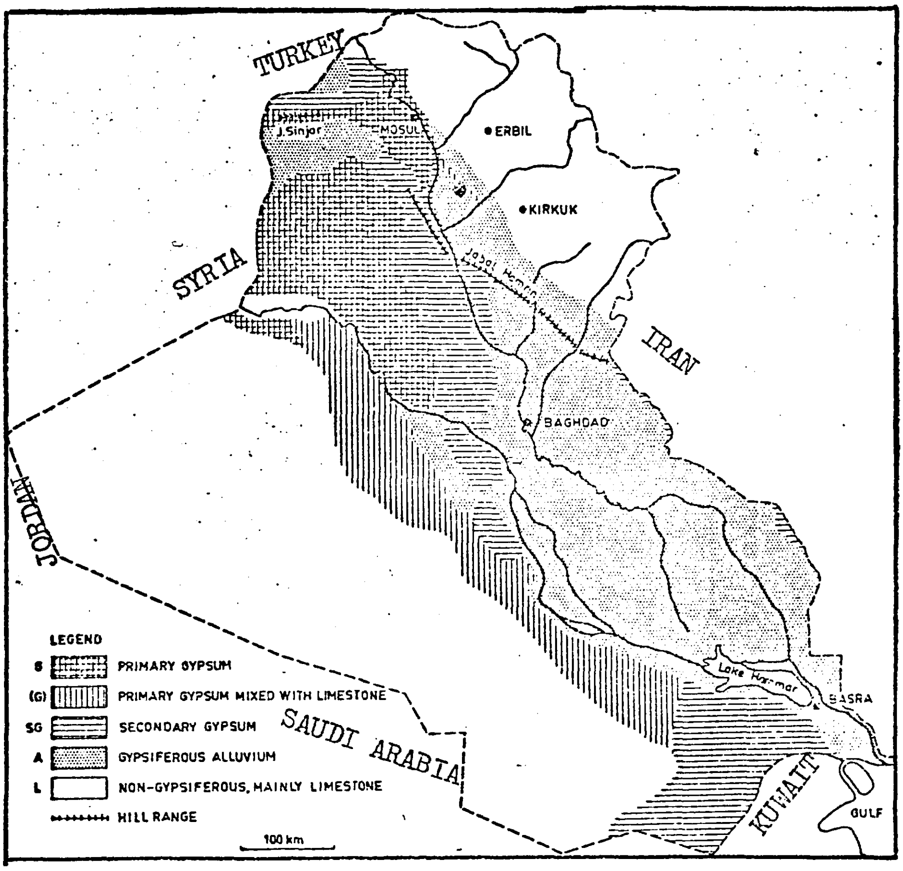


Fig. III Gypsum map of Iraq (data from various sources and own observations).

Scale 1: 1 000 000

Buringh (1960)

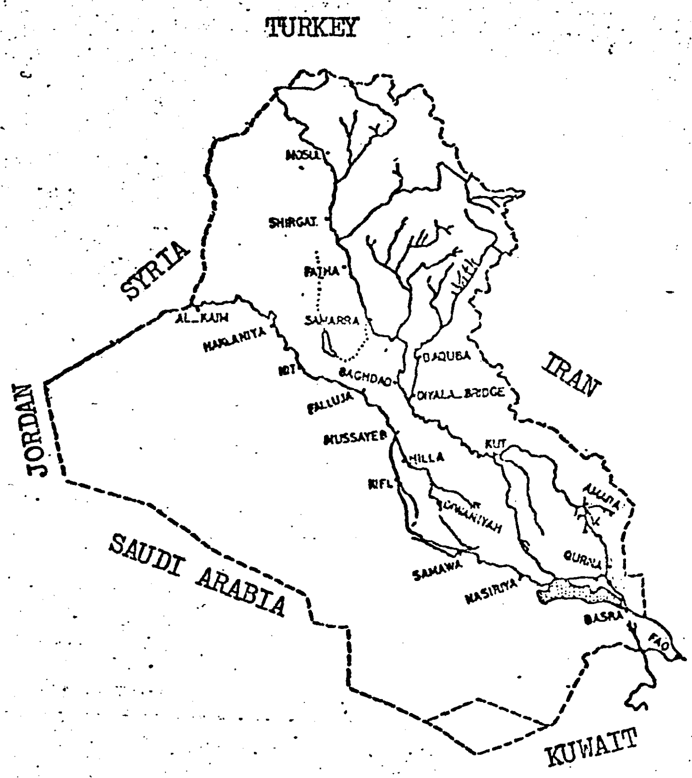


Fig. IV Map of Iraq showing water sampling sites

Scale 1: 1 000 000

Hanna _et al_ (1970)

CHAPTER TWO

LABORATORY METHODS AND INVESTIGATION

2.1 Soil chemical methods

2.1.1 Preparation of the samples:

The samples were collected at Higgins Neuck on the Forth estuary from three different sites :-

(1) River Forth, Pit No (1) beside the river. Two samples were taken, one from the top soil and one from the sub soil (12 inch depth).

(2) River Forth, Pit No (2) about 40 yards from the river. Samples were taken from the top soil and sub soil (12 inch depth).

(3) River Forth, Pit No (3) about 150 yards from the river on arable land above the flood plane level. Samples were taken from the top soil and from the sub soil (at a depth of only 6 inches, because of the stoney nature of the soil).

The characteristics of the soils were :-

Forth Pit (1)	Heavily mottled clay soil (gleyed soil)
Forth Pit (2)	Muck soil
Forth Pit (3)	Brown earth

The soil samples were taken from the field in July 1972. Then the samples were sieved wet through a 2 mm B.S.S. sieve and air-dried in the oven at 32°C.

2.1.2 Determination of moisture content:

The moisture content was determined according to the methods of analysis of the Association of Official Agricultural Chemists (1955).

2.1.3 Loss on ignition:

Loss on ignition was determined by igniting the soil at 700°C for 30 min., according to the methods of analysis of the Association of Official Agricultural Chemists(1955).

2.1.4 Water saturation percentage:

Water saturation percentage was determined according to Hesse (1971).

2.1.5 Determination of pH:

pH was determined according to Hesse (1971).

2.1.6 Sodium fluoride test:

The sodium fluoride test was carried out according to Fieldes and Perrot (1966).

2.1.7 Determination of soluble salts by saturation paste:

The saturation paste was carried out according to Allison (1973).

2.1.8 Determination of sulphate as barium sulphate:

This was carried out according to Vogel (1961).

2.1.9 Determination of chloride:

Chloride was determined according to Hesse (1971).

2.1.10 Determination of carbonate and bicarbonate:

Carbonate and bicarbonate were determined according to Hesse (1971).

2.1.11 Determination of gypsum:

Gypsum was determined by precipitation with acetone, according to Hesse (1971). Three different methods were used :-

(1) Extraction from saturation soil paste and precipitation by acetone (U.S. Salinity Lab. Staff (1954).

(2) Extraction from soil using a 1/20 soil/water ratio and precipitation by acetone, Hesse (1971).

(3) From the amount of calcium ion and sulphate ion, Hesse (1971).

2.1.12 Determination of cation exchange capacity and exchangeable bases:

Cation exchange capacity was determined according to U.S. Salinity Lab. Staff (1954) by shaking soil samples with M potassium acetate at pH 7 for 10 min. and then centrifuging until clear and the supernatant discarded. These steps were repeated three times, then the soil sample was shaken with 90% ethanol three times and the supernatant discarded as before. It was then extracted with M ammonium acetate at pH 7 three times and the leachate was collected and the volume made to 100 ml.

Exchangeable bases were determined according to U.S. Salinity Lab. Staff (1954) by extraction with M ammonium acetate at pH 7.

The individual elements were determined as follows :-

(1) Calcium and magnesium by atomic absorption spectrophotometry (Unican SP90).

(2) Sodium and potassium were measured by the E.E.L. flame photometer.

2.1.12.1 Standard curves :-

Standard curves were prepared for K, Na, Ca and Mg covering the range for sodium and potassium from 1 ppm to 10 ppm while for calcium the range was from 5 ppm to 20 ppm and for magnesium the range was from 0.5 ppm to 2 ppm.

5% La was used for calcium and magnesium to prevent interference from phosphate.

2.1.13 Organic matter:

Organic carbon was determined by the wet oxidation method (Walkley 1947).

2.1.14 Determination of lime:

$CaCO_3$ was determined by titration with 1 M NaOH after acidifying with 1 M HCl and boiling according to Jackson (1962).

2.2 Physical methods

2.2.1 Mechanical analysis (particle size distribution):

Samples were dispersed by ultrasonic treatment for 20 min. after oxidising the organic matter with 30% H_2O_2. The pipette method recommended by Edwards and Bremner (1967) was used for this determination.

2.2.2 Flocculation and dispersion experiment:

According to Van Olphan (1963), 1.0 gm of air dry soil sample was weighed and put into a 100 ml cylinder. Then 100 ml from a series of concentrations of salts, such as NaCl, Na_2SO_4, $CaCl_2$, $CaSO_4$, KCl, K_2SO_4, $MgCl_2$ and $MgSO_4$ were added and the suspension observed at intervals. This experiment was repeated with HCl, NaOH and $CaCO_3$ at 0.1 N concentration.

2.2.3 Permeability measurements:

Falling head permeameter was constructed according to Jumikis (1962) as shown in the diagram on page 60 . The permeability coefficient was calculated according to the same author.

2.2.4 Mineralogical analysis (optical examination):

Fractions of both coarse and fine sand were taken from each soil and the grains examined under a stereoscopic microscope.

2.2.5 Clay fraction (X-ray analysis):

Powder X-ray diffractometry was used to distinguish the different clays, Brown (1961).

The Fink A.S.T.M. index was used in the identification of the minerals.

2.3 Methods of plant analysis

2.3.1 Preparation of plant samples:

Plant samples were taken from the soil sites. These were exposed separately for four days in the laboratory to dry, then the samples were cut up and ground down to a fine powder.

2.3.2 Moisture content:

Moisture content was determined according to Piper(1950).

2.3.3 Total ash:

Plant samples were heated over a bunsen in a fume cupboard until they ceased smoking. The residue was transferred to a furnace at 450°C and heating continued for sixteen hours according to Piper(1950).

2.3.4 Determination of silica in plants:

Nitric acid was used to dissolve the ash, and after filtering made up to volume (250 ml). K , Na , P , Mg and Ca were determined in this solution. Phosphorus content was determined by the King's method (1932). K and Na were determined by flame photometry, and Mg was determined by atomic absorption spectrophotometry (SP90).

2.3.5 Determination of calcium:

Calcium was precipitated as calcium oxalate and the oxalate titrated with permanganate, Piper (1950).

2.3.6 Chlorine in plants:

The method of Husband and Godden (1927) was used for chlorine determination.

2.4 RESULTS AND DISCUSSION

2.4.1 The position and location of the soil samples taken for analysis were described in Chapter Two, Section 2.1.1. These samples had been flooded by estuarine water.

2.4.2 Physical properties of the soil (Field observation):

The soils which were flooded by the river were soggy under foot and when dried out in the laboratory they cracked. This could be related to a relatively high salt content.

Some permanent mottling was noted, both in the top and sub soil samples. On drying, the red mottles became more intense and the grey mottles became a deeper shade or black, which may be due to organic matter, or perhaps to some form of magnetite or manganese dioxide.

2.4.3 Consistency:

The samples which were flooded with sea water, i.e. gleyed soil samples, had a sticky consistency when wet, plastic when moist and firm when dry, while the consistency of the non-saline soil (brown earth soil sample) was friable.

2.4.4 Flocculation and dispersion:

These phenomena were studied by adding different concentrations of salts to the soil and observing the rate of precipitation. It was clear that in the case of the brown earth, which had a low initial monovalent salt concentration, coagulation took place on the addition of 1-5 meq/l of divalent cations, whereas flocculation did not occur with other soils which had higher initial monovalent salt concentrations, until a concentration of 40 meq/l of divalent cation had been added. This difference in the threshold limit for flocculation was due to the saline nature of the muck and gleyed soils, which were dispersed by the monovalent cations.

With increased salt concentration the suspension cleared more quickly, but with diluted salts more time was required for flocculation.

When NaOH was added to the soil the particles were dispersed. However, with the addition of HCl and $CaCO_3$ the solution became flocculated. The order of flocculation was as follows :-

$$\text{HCl} > \text{CaCO}_3 > \text{control} > \text{NaOH}$$

When these effects occur the net results, as revealed by mechanical analysis, are high figures for silt and low figures for clay. This is related to the aggregates of clay which have been fractionated as silt.

Colloidal substances such as silica and humus which occur in the soils are precipitated from their solution or sols by calcium and other alkaline earth compounds, when the medium is alkaline, but not when the medium is neutral or acid.

2.4.5 Optical examination:

The grains of soil were examined; the light material was believed to be dominated by Quartz and Feldspar while the dark minerals were probably iron oxide or iron rich silicates.

2.4.6 Permeability:

The permeability of gleyed soil after saturation was lower than that of the brown earth soil, despite having greater amounts of organic matter. This effect was probably due to the higher percentage of exchangeable sodium in the saline soils, which dispersed the soil particles, and allowed the fine particles to clog the pores between the larger aggregates as shown in Table (2.2).

2.4.7 % loss of moisture:

The percentage moisture loss of the muck and gleyed soil was lower than of the brown earth. This may have been due to oxidation of metals in the muck and gleyed soil partly compensating for the moisture loss.

The percentage loss in moisture increased with depth for all the samples as shown in Table (2.3).

2.4.8 Mechanical analysis:

The particle size distribution of these soils indicate a high content of silt with a very small sand fraction.

The results show that both top and sub soils of the brown earth have a slightly higher percentage of silt and sand, and a lower percentage of clay than gleyed top and sub soils.

Brown earth top and sub soils have a greater percentage of sand and a similar or slightly lower percentage of silt and clay compared to muck soil.

It clearly appeared from the results that for all the soils the clay content increased with depth as shown in Table (2.12).

The silt fraction was found to be inversely proportional to the clay content in both gleyed and brown earth soil, but in muck soil it increased along with the clay content.

The sand fraction decreased with increasing depth except in brown earth. It was concluded from the above that the soils of these samples were characterised by a high content of clay and silt and a low sand content.

2.4.9 Clay fraction (X-ray analysis):

The X-ray diffraction films indicated that in all of the Forth soil samples Kaolinite and expanding clay at 14.46 Å were identified.

The expanding clay could be chlorite or montmorillonite When the clay fraction was heated to 550°C the presence of illite in the soil was confirmed. It seemed to be the dominant clay mineral. Kaolinite was identified by the disappearance of the 7.1 Å on heating to 550°C. This suggests that almost certainly, there was Kaolinite in the soils.

The X-ray diffraction films also indicated that the 3.35 Å line for Quartz was present. The 2.56 Å line suggested the presence of illite as shown in Table (2.13).

2.4.10 Samples of the standing water:

Samples of the standing water on the soil samples in this area were taken and the chemical composition of this water was investigated.

Sodium was the most abundant cation, it was very high, as shown in Table (2.5). It was 200.2 meq/l.

Chloride was the predominant anion, it was also very high, as shown from results. It was 120.2 meq/l. Potassium was usually the least abundant. Divalent cations were present to a lesser extent than sodium. Magnesium concentration was 8.6 meq/l and 0.8 for calcium.

Magnesium was more important than calcium (see Table (2.5) for full details). The order of cation concentration was :-

$$Na > Mg > Ca > K$$

The water had a high salinity and low alkalinity. The high water salinity was due to the presence of $NaCl$ and $MgCl_2$ in high concentrations, but the low alkalinity was may be due to the contact with the CO_2 from the atmosphere which could reduce the pH to 6.8.

Gypsum was present in significant amounts and the phosphate level was high. It was 3.7 meqP/100 ml. This may be because of the presence of untreated sewage dumped into the Forth estuary, e.g. detergents.

2.4.11 Chemical analysis of plants:

The marsh plants grown on the muck and gleyed soil contained small amounts of Ca and K but high amounts of Na, Mg and Cl , compared with plants grown on the brown earth, as shown in Table (2.6).

A calculation of 0.2%, 0.3% for Ca and 1.0%, 1.3% for K based on dry matter in gleyed soil and muck soil respectively was obtained, but contents of 0.5%Ca and 2.3%K were obtained in plants grown on the brown earth.

Negligible amounts of Na were found in plants grown on the brown earth (0.4%), while substantial amounts were found in plants grown on marshy soil (gleyed and muck soil) (3.5% and 3.7%), Table (2.6).

The plants from muck and brown earth soils have approximately the same amount of phosphate. The plants from these soils contain higher amounts of phosphate than the plants for gleyed soil, as shown in Table (2.6).

The plants from gleyed and muck soils have 2.0% and 7.0% silicate in the dry matter respectively; the plants from brown earth soil contain 20.0% silicate in their dry matter.

The plants from gleyed and brown earth soils have about the same amount of ash but greater amounts than plants grown on muck soil.

2.4.12 Chemical properties of soils:

A number of chemical parameters of the soil samples were measured at different soil/water ratios. Saturated soil paste, 1:5 and 1:10.

The different ratios were used to give more information on the salt content of the soils and to investigate the effect of different soil/water ratios on the mobilization of ions.

2.4.12.1 Determination of pH :-

The pH of the soils and extracts in different soil/water ratios were measured and the extracts were found to be less acidic than the suspension. This is an example of acid suspension effect which may be explained by Donnan equilibrium theory. One explanation of this effect has been given by Mattson (1931).

The saline soils had higher pH than the non saline soils as shown in Table (2.7). This may be due to the presence or absence of CO_3 which will give greater variation in pH.

2.4.12.2 Percentage organic matter :-

The organic content of the gleyed soil was higher than that of the muck soil, and brown earth. In sieving the soil the roots and most of the associated organic matter was removed from the muck soil which explained why it had a lower content of organic matter than gleyed soil, as shown in Table (2.3). It was 9.6% to 13.5% organic matter for the gleyed soil, but it was 5.5% to 8.3% for the muck soil and 5.5% to 7.6% for the brown earth.

2.4.12.3 Sodium fluoride test :-

The change in the pH of the soil suspension was not significant. The slight increase in the pH was due to the free OH ions which are gradually released as the fluoride comes into contact with the alumina silicate. The NaF test showed that very little non-crystalline alumina silicate was present. pH values more than 10.0 suggest the presence of amorphous alumina silicate, but no such pH changes were noted.

2.4.12.4 Conductivity :-

The conductivity of the saline soils was higher than for brown earth soil sample (control), as expected, while the top soils had lower conductivity than sub soils. This may be related to the organic matter in the top soil immobolizing ions, and to the higher concentration of cations in the sub soil.

2.4.12.5 Determination of soluble salts :-

The sub soil was found to have higher contents of soluble salt than the top soil. This is possibly due to the same reason given previously which is related to the organic matter. In both the muck and gleyed soils, which had been flooded with sea water, Na and Cl were the dominant ions.

The range found was 38.3-41.7 meq Na/100 gm oven dry soil, 36.0 - 41.0 meq Cl/100 gm oven dry soil for gleyed soil, while the range was 20.4 - 20.6 meq Na /100 gm oven dry soil, 23.0 - 24.0 meq Cl/100 gm oven dry soil for muck soil.

However Mg and SO_4 were present in lower amounts. The range found was 1.5-4.0 meq Mg/100 gm oven dry soil, 1.6-4.9 meq SO_4/ 100 gm oven dry soil for gleyed soil, while the range was 1.9 - 2.2 meq Mg /100 gm oven dry soil sample, 1.0 - 1.1 meq SO_4 /100 gm oven dry soil sample for muck soil, as shown in Table (2.8).

Similar amounts of calcium were found in both saline and none salin soils, but in the brown earth, Ca and Mg were the predominant cations, with lower amounts of Na and K as might be expected.

The full results are shown in Table (2.8), and the full results for extracts of saturation paste are shown in Table (2.9).

2.4.12.6 Determination of extractable phosphorus :-

The phosphate concentration was 2.6 - 4.4 meq/l which is in the region normally expected for arable soils. The extractable phosphate concentration was high in all the soils. The general dominance of phosphate is more pronounced in the top soil and decreases with depth in both gleyed and muck soil. Similar results were obtained with the brown earth soil.

This may be related to the higher salt concentration in the sub soil which increases the retention of phosphate by the soil, and makes it insoluble , as shown in more detail in Chapter Three.

The full results for extractable phosphate are presented in Table (2.9).

2.4.12.7 Determination of exchangeable cations and C.E.C. and total exchangeable bases :-

The saturation of the clay with Ca was higher in the brown earth than in the saline soils. The range was 11.7-13.4 meq Ca / 100 gm oven dry of brown earth soil sample, but it was 4.1 - 4.6 meq Ca /100 gm oven dry of muck soil and 5.6 - 5.8 meq Ca /100 gm oven dry gleyed soil sample. Mg , Na and K levels were higher in the saline soils.

The range was 7.4-7.6 meq Mg, 10.3-11.4 meq Na and 2.5-2.7 meq K/100 gm oven dry for muck soil, while the range in gleyed soil was 11.6 - 12.0 meq Mg , 9.2 - 11.9 meq Na and 2.5 - 4.3 meq K/100 gm oven dry soil.

In brown earth soil sample the range was 3.1 - 3.3 Mg , 0.4 - 0.4 Na and 1.5 - 1.6 meq K/100 gm oven dry soil sample.

The higher saturation of the clay with Ca in the brown soil when measured by extraction with ammonium acetate may be related to the liming of the soil. The cation exchange capacity of the gleyed soil samples was higher than for the other two.

It was 28.8 - 30.0 meq cation/100 gm oven dry soil for brown earth, 28.0 - 28.1 meq cation/100 gm oven dry soil for muck soil and 34.8 - 40.8 meq cation/100 gm for gleyed soil, as shown in Table (2.10).

The total exchangeable bases for the saline soils were higher than for the brown earth soil.

2.4.12.8 The exchangeable sodium percentage :-

The exchangeable sodium percentage was higher in the saline soils, as was the soluble sodium percentage, as shown in Table (2.10).

2.4.12.9 Determination of % lime :-

The percentage lime content of the sub soil was found to be higher than top soil and it was higher in the brown earth than in saline soil, as shown in Table (2.11). This may be related to the liming of the soil.

2.4.12.10 Gypsum :-

The available data, Table (2.4) indicates that the gypsum content usually increased with depth and that higher values were generally found close to the river.

The amount of gypsum liberated was less at high dilution than from the saturation paste. This was possibly because the shaking time of 30 min. used at high dilution was insufficient for equilibrium to be reached between soil-bound and dissolved gypsum, despite the greater water/soil ratio.

The amounts of gypsum present in the brown earth soil were low, with the exception of brown earth sub soil in 1:5 soil/water ratio. It was 1.3 meq/l. This could be due to fertilizer treatments.

Generally, with the exception of muck sub soil (0.1 meq/l) and gleyed top soil (0.2 meq/l), gypsum levels were high in gleyed and muck soils for both top and sub soil samples.

Table (2.1)

Solubility of salt in distilled water

Hodgman *et al* (1960)

gm/100 ml of water

Cation	Cl		SO_4		CO_3	
	Cold	Hot	Cold	Hot	Cold	Hot
Na	35.7	39.12	4.76	42.7	7.1	
K	34.7	56.7	6.85	24.1	0.11	
Ca	59.5	15.9	0.241	0.222	0.0014	0.0018
Mg	54.25	72.7	26.0	73.8	0.011	

Table (2.2)

Rate of flow of water through soil (permeability in cm/sec,)(Donahue et al 1971)

Aliquots	Gleyed soil	Muck top soil	Muck sub soil	Brown earth top soil	Brown earth sub soil
Unsaturated 1st	30.0×10^{-4}	11.0×10^{-4}	5.8×10^{-4}	1.7×10^{-4}	4.7×10^{-4}
Unsaturated 2nd	49.0×10^{-4}	3.7×10^{-4}	1.2×10^{-4}	1.2×10^{-4}	1.2×10^{-4}
Saturated soil 24 hours			0.5×10^{-4}	1.2×10^{-4}	1.0×10^{-4}
Saturated soil 36 hours			0.3×10^{-4}	1.1×10^{-4}	1.0×10^{-4}
Waterlogged 48 hours			$< 0.1 \times 10^{-4}$	1.0×10^{-4}	0.5×10^{-4}
Waterlogged 72 hours			$< 0.1 \times 10^{-4}$	1.0×10^{-4}	0.5×10^{-4}

Permeability classes of soil (Donahue et al 1971)

Very low	$< 1.4 \times 10^{-4}$ cm/sec
Slow	$(1.4 - 4.4) \times 10^{-4}$ cm/sec
Moderate	$(4.4 - 14.0) \times 10^{-4}$ cm/sec
Rapid	$(14.0 - 44.0) \times 10^{-4}$ cm/sec
Very rapid	$> 4.4 \times 10^{-4}$ cm/sec

Table (2.3)

Moisture and organic matter contents of soil

	% loss moisture	factor	% loss ignition	% C	% O.M. C x 1.72	% S.P.
Gleyed top soil	3.4	0.966	22.8	7.6	13.5	100.0
Gleyed sub soil	6.1	0.939	15.5	5.6	9.6	98.0
Muck top soil	4.3	0.958	13.7	4.2	8.3	90
Muck sub soil	4.9	0.95	10.5	3.3	5.5	88
Brown earth top soil	14.6	0.854	9.4	4.3	7.6	98
Brown earth sub soil	14.8	0.852	7.4	3.1	5.5	90

S.P. = Water saturation percentage

Table (2.4)

Determination of Gypsum (Hesse 1971)

meq/1

	Total gypsum 1:20	Total gypsum in sat. paste
Gleyed top soil	0.8	0.2
Gleyed sub soil	0.9	2.1
Muck top soil	0.7	1.1
Muck sub soil	0.1	1.2
Brown earth top soil	0.2	0.1
Brown earth sub soil	1.3	0.1

Table (2.5)

Total chemical analysis for standing water

EC mmhos/cm at 25°C	Salt ppm	pH	% gypsum	Na	K	Ca	Mg	Cl	HCO_3	P	SO_4
										meq/l	
5.9	3781	6.8	0.9	200.2	0.3	0.8	8.6	120.2	1.2	3.7	0.1

Table (2.6)

Total chemical analysis of plant % dry matter

Plant		% moisture	% ash	SiO_2	PO_4	Cl	SO_4	Na	K	Ca	Mg
								% dry matter			
Marsh	Gleyed soil	10.6	31.9	2.0	0.1	4.9	0.7	3.5	1.0	0.2	0.6
	Muck soil	10.8	22.0	7.0	0.2	4.9	2.8	3.7	1.3	0.3	0.4
Grass	Brown earth soil	9.5	32.9	20.0	0.2	2.0	0.4	0.4	2.3	0.5	0.2

Table (2.7)

Actual pH value for soil at different soil water ratios

	Extract of saturation paste	Suspension of $CaCl_2$ 1:2.5	Suspension of H_2O 1:2.5	Extract of soil water 1:2.5	Suspension of soil water 1:5	Extract of soil water 1:5
Gleyed top soil	6.8	6.7	6.8	7.1	6.9	7.4
Gleyed sub soil	7.7	6.8	6.9	7.0	7.1	7.2
Muck top soil	6.9	6.6	6.7	6.8	6.8	7.0
Muck sub soil	6.6	6.7	6.9	6.9	7.0	7.1
Brown earth top soil	7.0	5.6	5.9	6.7	6.8	6.9
Brown earth sub soil	7.6	5.5	5.8	6.2	6.4	6.7

Table (2.8)

Total soluble salts in soil - 1:5 soil water ratio

		Soluble cations meq/100 gm oven dry soil							Soluble anions meq/100 gm oven dry soil			
	EC mmhos/cm	Na	K	Ca	Mg	Total	S.A.R.	S.S.P.	Cl	HCO_3	SO_4	meq/l P
Gleyed top soil	10.1	38.3	1.3	0.2	1.5	41.3	40.9	1243	36.0	0.5	4.9	4.4
Gleyed sub soil	10.6	41.7	1.6	0.4	4.0	47.7	28.2	694	41.0	0.5	1.6	2.6
Muck top soil	5.4	20.4	0.7	0.5	2.2	24.1	17.9	624	23.0	1.1	1.0	3.8
Muck sub soil	6.3	20.6	0.7	0.4	1.9	23.5	14.3	695	24.0	0.6	1.1	2.2
Brown earth top soil	0.2	0.5	0.3	0.2	0.1	1.1	1.2	78	2.0	0.6	1.1	2.6
Brown earth sub soil	0.2	0.8	0.3	0.6	0.3	2.0	1.2	67	1.0	2.3	0.2	2.8

Ec = electrical conductivity

S.A.R. = Sodium Adsorption ratio

S.S.P. = Soluble Sodium percentage

Table (2.9)

Total solublesalt conductivity. S.A.R., S.S.P. in soil saturation paste

		Soluble cations meq/100 gm oven dry soil							Soluble anions meq/100 gm oven dry soil		
	EC mmhos/cm	Na	K	Ca	Mg	Total	S.A.R.	S.S.P.	Cl	HCO_3	SO_4
Mick top soil	37.2	33.0	1.1	1.0	7.2	42.3	16.4	355.9	42.6	0.6	6.6
Mick sub soil	53.2	49.2	1.3	1.0	9.6	61.1	21.3	410.9	53.3	1.7	3.1
Gleyed top soil	34.1	25.5	0.6	0.7	5.4	32.2	14.7	385	32.3	1.2	2.3
Gleyed sub soil	42.9	24.9	0.7	0.6	5.3	31.5	14.4	375.2	31.8	0.3	2.7
Brown earth top soil	0.6	0.2	0.1	0.1	0.1	0.5	0.6	65.2	0.3	0.2	0.1
Brown earth sub soil	0.5	0.1	0.1	0.1	0.1	0.4	0.0	24.5	0.1	0.2	0.1

E.C. = Electrical conductivity

S.A.R. = Sodium adsorption ratio

S.S.P. = Soluble sodium percentage

Table (2.10)

Determination of exchangeable cationsand C.E.C. of soil

	Exchangeable cations meq/100 gm oven dry soil				meq/ 100 gm oven dry soil				
	Ca	Mg	Na	K	Total bases	E.S.P.	C.E.C.	% base cation	meq/1 Ca
Gleyed top soil	5.6	11.6	9.2	2.5	28.8	26.3	34.8	83.0	19.5
Gleyed sub soil	5.8	12.0	11.9	4.3	34.0	29.2	40.8	83.0	17.1
Muck top soil	4.6	7.6	11.4	2.7	26.2	45.2	28.1	93.3	17.4
Muck sub soil	4.1	7.4	10.3	2.5	24.2	36.8	28.0	86.7	16.8
Brown earth top soil	13.4	3.1	0.4	1.5	18.4	1.2	30.0	61.6	12.9
Brown earth sub soil	11.7	3.3	0.4	1.6	16.9	1.3	28.8	58.7	69.5

Table (2.11)

% Lime $CaCO_3$ Jackson (1962)

	% Lime
Gleyed top soil	1.6
Gleyed sub soil	2.8
Muck top soil	2.6
Muck sub soil	2.6
Brown earth top soil	3.3
Brown earth sub soil	3.8

Table (2.12)

Mechanical analysis soil separation fraction by pipette method

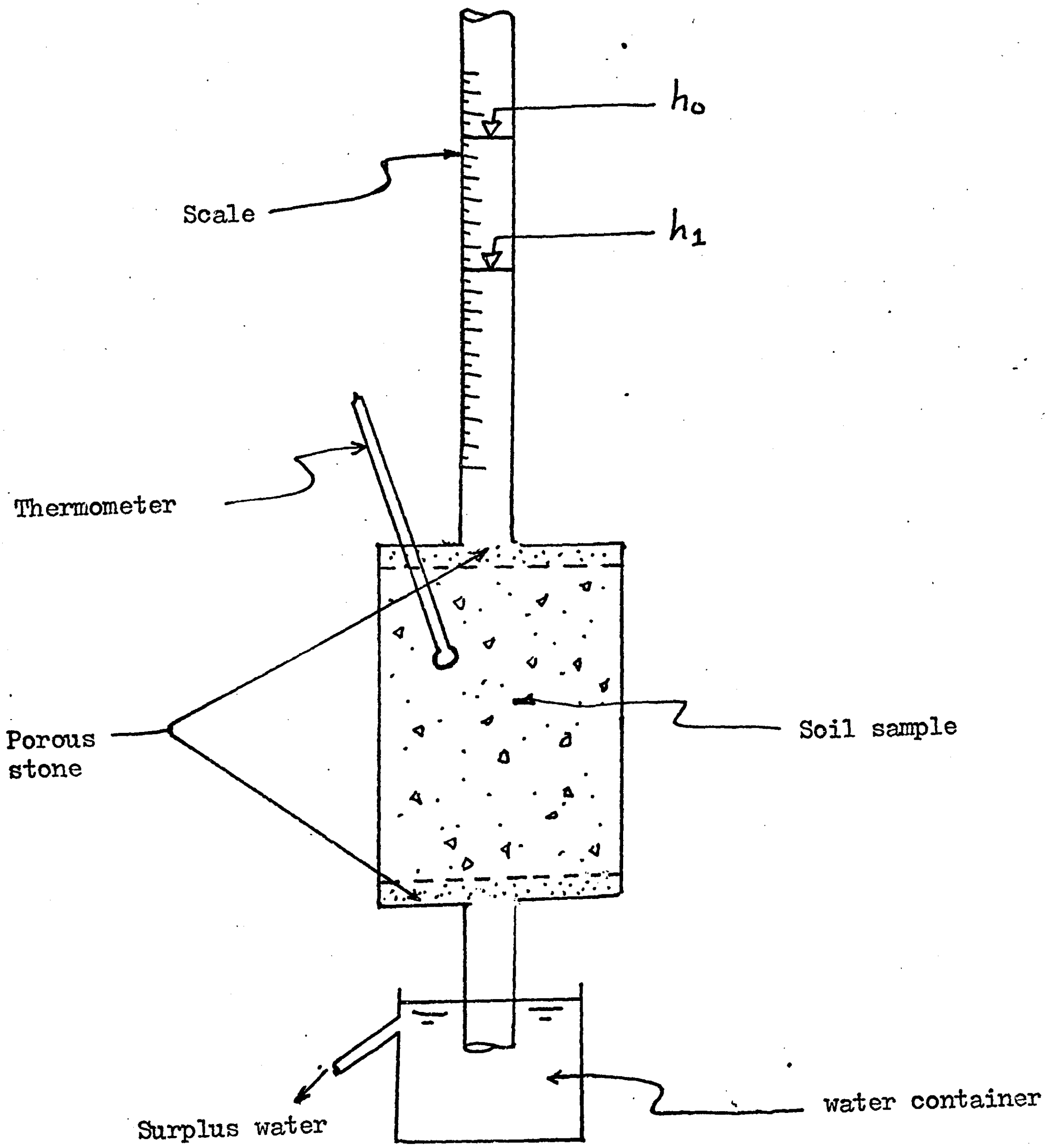
	% Sand	% Clay	% Silt	Texture classes
Gleyed top soil	2.0	41.3	56.9	Silty clay loam
Gleyed sub soil	0.6	46.3	52.1	Silty clay
Muck top soil	6.1	29.3	64.6	Silty clay loam
Muck sub soil	4.3	32.3	67.7	Silty clay loam
Brown earth top soil	7.2	28.2	64.6	Silty clay loam
Brown earth sub soil	8.6	32.7	58.8	Silty clay loam

Table (2.13)

X-ray Spacing Table

Gleyed soil				Brown earth soil			
4θ	2θ	Reading (Å)	Mineral	4θ	2θ	Reading (Å)	Mineral
14.0	7.0	14.76	Expanding clay	14.0	7.0	14.46	Expanding clay
21.0	10.5	9.8	Illite	21.0	10.5	9.8	Illite
29.0	14.5	7.1	Kaolinite	29.0	14.5	7.1	Kaolinite
26.0	23.0	4.49	Kaolinite & Illite	42.0	21.0	4.91	Kaolinite & Illite
49.0	24.5	4.22		50.0	25.0	4.14	
58.0	29.0	3.57		58.0	29.0	3.54	
62.0	31.0	3.35	Quartz	62.0	31.0	3.55	
71.0	35.5	2.94		66.0	33.0	3.15	
82.0	41.0	2.56		82.0	41.0	2.56	

FALLING HEAD PERMEAMETER



LEGEND

h_o = The level of water at the beginning of the test

h_i = The level of water at the end of the test

DIAGRAM

CHAPTER THREE

PHOSPHATE

3.1 INTRODUCTION

3.1.1 Origin of phosphate:

The native phosphate in soil is either organic or inorganic. The organic fraction constitutes 20 - 80% of total soil phosphorus. It is only after mineralization of the organic phosphates (activity of micro-organisms) that it becomes involved in the chemical reaction (Larsen 1967).

However, in Scottish soils organic formscan account for more than 50% of the total phosphorus. This ratio is lower in soils developed under conditions of impeded drainage (Williams 1970). It has been shown in Scottish soils that a major influence on the content of inorganic phosphate is the pedological drainage condition in addition to the parent material.

Inorganic phosphate is that resulting from the disintegration and decomposition of rocks containing apatite $Ca_{10} (PO_4)_6$ (F, Cl, OH, $\frac{1}{2}$ CO_2) (Tyrrol 1971; Smeck 1973). This occurs as primary apatite in sand and silt fraction. Much of the inorganic phosphate consists of a variety of amorphous complexes and compounds of varying crystallinity, which exist probably as films and deposits on other soil constituents.

There is iron phosphate (Virianite $Fe_3 (PO_4)_2 8H_2O$), which is found in waterlogged or badly drained soils, also aluminium phosphate, (3 Al (OH), $2PO_4$ - $3H_2O$ Sturrettite and Variscite Al PO_4 - $2H_2O$) (Russell 1961).

Tribasic orthophosphate forms three series of salts according to the number of hydrogen atoms replaced in the molecule. Monocalcium phosphate has the highest water solubility. Tricalcium phosphate is insoluble and dicalcium phosphate ($CaHPO_4$) is intermediate.

$$Ca(H_2PO_4)_2 \rightleftharpoons CaH\ PO_4 \rightleftharpoons Ca_3(PO_4)_2$$

Under acid conditions, the equilibrium moves to the left, but as the pH increases the more insoluble compounds become dominant. Around neutrality monocalcium phosphate would probably be the principle stable compound. Under more alkaline soil conditions tricalcium phosphate is present and more basic and insoluble phosphates of calcium such as calcium octaphosphate ($Ca_4H(PO_4)_3$ $3H_2O$) and hydroxyl apatite (3 $Ca_3(PO_4)_2$ $Ca(OH)_2$ are also likely to be present.

3.1.2 Phosphorus in soil solution:

The inorganic phosphorus in solution takes part in two equilibria — homogeneous and heterogeneous equilibria. The first one occurs in the liquid phase, but the second between the solid and liquid phase.

1. Homogeneous equilibrium. The concentration of phosphorus in the liquid phase depends on the properties of both the solid and liquid phase and also on the ratio between solid and solution.

The forms of phosphorus present in solution are governed by protonation and complex formation. These forms are H_3PO_4, $H_2PO_4^-$, $HPO_4^{=}$ and $PO_4^{\equiv}$ and their soluble complexes.

(a) Protonation is the distribution of phosphorus between phosphoric acid and phosphorus ions which is determined by pH as follows :-

$$P_{acid} \rightleftharpoons P_{base} + H^+$$

$$K = \frac{[P_{base}][H^+]}{[P_{acid}]}$$

K = dissociation constant which is influenced by temperature and concentration of the solution

By using activities $[a]$ the equation is as follows :-

$$pKa = PH - \log \frac{[a] P_{base}}{[a] P_{acid}}$$

Thus the concentration of various phosphate ions in solution is intimately related to the pH of the media (Vogel 1961). The shape of the buffer curve of phosphoric acid will depend upon the relative magnitudes of the various dissociation constants for tribasic acids, which are illustrated for orthophosphoric acid. This acid behaves as a mixture of three monobasic acids, with dissociation constants for which

$$H_3PO_4 \rightleftharpoons H_2PO_4^{-} \rightleftharpoons HPO_4^{=} \rightleftharpoons PO_4^{\equiv}$$

$$pK_1 = 2.12 \qquad pK_2 = 7.21 \quad pK_3 = 12.30$$

(b) Complex formation:

Phosphorus forms soluble complexes with many metallic ions such as Na, K, Mg, Ca, Mn, Al and Fe (Sillen and Martell 1964). With the soluble complexes and their equilibrium constants, expressed as stability constants, the greater the constant, the more stable is the complex.

Soil solution normally contains several kinds of metallic ions which will form complexes with ions other than phosphate (OH , CO_3 , SO_4 and organic ions).

In addition, phosphorus ions may take part in other homogeneous reactions (Larsen 1967).

2. <u>Heterogeneous equilibrium</u>. The upper limit for the phosphorus concentration in solution is set by the heterogeneous equilibria. The reactions involved (dissolution and precipitation) are controlled by the solubility product principle and adsorption of phosphate on the surface of soil particles.

(a) Solubility:

It was concluded (Wild 1964; Chakravarti and Talibudeen 1962; Hagin and Hadas 1962; Bache 1963) that the phosphorus concentration in the soil solution does not agree with that predicted from the solubility product. This disagreement however, in calcureous soils can be explained by incomplete understanding of the solubulity product of these compounds (Bjerrum 1949). Two solubility products were found for octocalcium phosphate and two for hydroxyl apatite, one where the equilibrium was approached by precipitation and the other when it was approached by dissociation.

However, impurities seem to have an effect on the solubility such as the change in the solubility of hydroxyl apatite in the presence or absence of calcium carbonate (Greenwald 1942).

(b) Adsorption. Phorphorus can be adsorbed on the surface of soil particles such as clay or calcium carbonate. Thus phosphorus can be removed from solution even in the absence of precipitating ions.

Phosphorus adsorption was investigated (Muljadi et al 1966) over a pH range from 3 to 10 and an initial phosphorus concentration from 10^{-5} to 10^{-1} M, by using clay (Kaolinite) and two aluminium oxides (Gibbsite and Bentonite). They found three distinct adsorption concentration ranges :-

(i) At low concentration of phosphorus 10^{-4} M.
(ii) At intermediate phosphorus concentrations 10^{-4} - 10^{-3} M.
(iii) At medium to high phosphorus concentrations 10^{-3} - 10^{-1} M.

They then suggested that aluminium atoms located on the edge of the crystal lattice are responsible for phosphorus adsorption in ranges (i) and (ii). In range (iii) when the adsorption isotherms were linear, phosphorus was found to penetrate into some amorphous regions of the crystals.

It was indicated (Larsen 1967) that lower phosphorus concentrations are relevant to intact soil, while the more concentrated solutions are relevant to soil which comes into contact with the solution from dissolving fertilizers.

3.1.3 The availability of phosphate:

The bulk of the soluble phosphorus in soil is always present as the two ion species $H_2PO_4^-$ and $HPO_4^=$ (Larsen 1967).

The calculation of Buehrer (1932) shows that the predominant anion in the pH range of most soils is $H_2PO_4^-$. This form $H_2PO_4^-$ was considered to be the usable form by plants.

The concentrations of this ion in the soil solution is considered to be small, i.e. generally not more than a few ppm and frequently less than 1 ppm. It is obvious that the concentration varies widely for different soils. The soil is known to be deficient in phosphate when its concentration is from below 10^{-7} M to about 10^{-6} M, and it is known to be well supplied for crops to grow to maturity at concentrations $10^{-6} - 10^{-4}$ M. (Russell 1961).

The ability of crops to take up phosphate from these dilute solutions however is dependent to some extent at least on the absence of some interfering ions, such as high concentrations of ferric oxide which reduce the translocation of phosphate to the leaves (Foster and Russell 1958). This effect can also be produced by aluminium ions (Wright & Donahue 1953).

There are four main considerations in respect of the supply of phosphate to crops. These are :- (Williams 1970).

(i) The quantity factor which represents the amounts of available phosphate to the plant.

(ii) The intensity factor which reflects the strength of retention of phosphate by the soil and hence the effort required to withdraw it.

(iii) The quantity/intensity relationship factor. This relationship is defined by the adsorption isotherm and expresses the phosphate buffering capacity of the soil.

(iv) The rate factor covering replenishment of the phosphate in the solution around the plant roots.

3.1.4 Donnan equilibrium:

Acidoid and basoid behaviour governs the composition of the miceller atmosphere. According to Mattson (1929) the electronegative soil is composed of particles with a negatively charged surface represented by the layer of acidoid anions surrounded by a swarm or atmosphere of exchangeable cations.

The thickness of this atmosphere of ions is determined by a balance between the inward acting electrostatic attraction and the outward acting osmotic force tending towards an equal distribution of the ions.

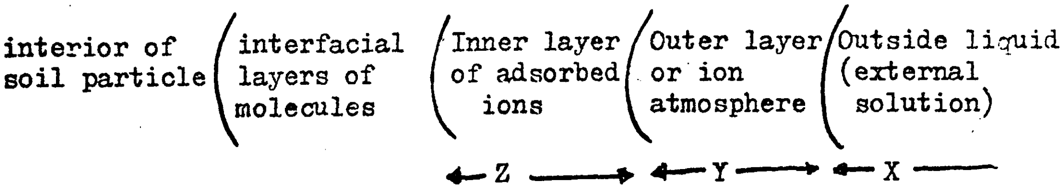
Soil is a colloidal system in which the solid or colloidal phase is surrounded by an inner solution containing an excess of one kind of ion (exchangeable cations) and an outer solution containing only the ions of the free electrolytes. The Donnan equation demands that at equilibrium the product of the concentration of any pair of diffusible ions must be the same in any part of the system (Mattson 1966).

There is a concentration X of the free ions in the inter miceller solution while in the miceller solution there is a concentration Y of the free ions. There is also a concentration Z of ions belonging to the micelle which depends on the charge of the colloid.

If it is electronegative Z = H or a metal cation, but if it is electropositive Z = OH or other anion.

The application of the Donnan theory gives the general equation for a uni-univalent ion.

$$X^2 = Y\ (Y + Z)$$



The activity of counter ions decreases rapidly from the particle surface outwards, whereas the activity of the free salts increases in the same direction.

The theoretical distribution of the ions in Donnan system depends on :-

(1) The activity of the solution (X)

(2) The valence of the anions and cations

(3) The exchange capacity of soil (Z)

When the soil solution is diluted, there will be a Donnan redistribution of the ions from the inside solution Y to the outside solution X. But Y tends to be constant due to the equilibrium between the dissolved phosphate Y and the adsorbed phosphate S, as illustrated:-

$$S \rightleftharpoons Y \rightleftharpoons X$$

The salt effect is

$$S \overset{\rightharpoonup}{\longleftarrow} Y \overset{\rightharpoonup}{\longleftarrow} X$$

This relationship is unique for the phosphate ion. The other anions such as Cl , NO_3 and SO_4 are not adsorbed by soil colloids to any great extent, and exist in soil solution. This could be related to the adsorption of phosphate onto the surface of clay particles and takes place by hydrogen bonding anion exchange, or chemisorption (chemical bond.); but for other anions adsorption is related only to the electrostatic attraction, its concentration in the soil atmosphere presumably being affected by any factor which influences the equilibrium.

The phosphate saturation S is in equilibrium with Y the inside activity of the $H_2PO_4^{-}$ ion. With no added salt and with higher exchange capacity Z of the soil Y is smaller than X. When salt is added the difference between X and Y decreases by transfer of ions from X to Y. This disturbs the equilibrium of S.

In electronegative colloids it can be concluded that the valence affects the distribution of cations as well as anions between the inside and outside solution. It is expressed by the general equation :-

$$- - - \quad \frac{\sqrt[3]{(A^{---})_i}}{\sqrt[3]{(A^{---})_o}} = \frac{\sqrt{(A^{--})_i}}{\sqrt{(A^{--})_o}} \quad \frac{(A^{-})_i}{(A^{-})_o}$$

$$= \quad \frac{(M^{+})_o}{(M)_i} \quad \frac{\sqrt{(M^{++})_o}}{\sqrt{(M^{++})_i}} \quad \frac{\sqrt[3]{(M^{+++})_o}}{\sqrt[3]{(M^{+++})_i}}$$

(Z + Y) is substituted for $(\quad)_i$

(X) is substituted for $(\quad)_o$

(1) There is always less of the free electrolyte in the inside than in the outside solution, i.e. $Y < X$.

(2) The ratio $\frac{Y}{X}$ decreases with the dilution of the solution, at infinite dilution, the free electrolyte is limited to the ions of the water.

(3) A high concentration of salt solution suppresses the Donnan distribution and the ratio Y/X approaches unity.

(4) The higher the value of Z (the exchange capacity), the higher the concentration of salt required to suppress the Donnan distribution.

In concentrated solution, there is little or no valence effect, but on dilution of the solution and a high exchange capacity adsorption of cations and desorption of anions is affected by valence.

Mattson (1929) found, that the dissociation of the cations depends not only upon the valence but also upon other factors, amongst which atomic volume and the degree of hydration of the ions appear to be most important (specific nature of ions).

The smaller the volume of the cation, the greater the hydration, (the greater the number of water molecules attached to the ion) then the smaller is the potential and the more insensitive the cation to electrostatic pull from the surface.

The higher the valence and the lower the hydration, on the other hand, the more easily the ion is attracted to the inner layer of opposite charge.

In this situation the ions arrange themselves in the well known Hofmeister or lyotropic ion series.

This theory also explains why the magnitude of the positive salt effect on the phosphate adsorption is related more to the contents of acidoids than basoids. Z is determined by the acidoid, and a high Z means a great different between X and Y and a large effect of the salt on $\frac{XP}{YP}$ ratio.

For the same reason the positive salt effect is large at high pH, decreasing to zero with falling pH, and eventually reversing into a negative effect.

This phenomena is explained by the fact that Z decreases in the same direction and that the saloid-bound phosphate increases with the acidity.

The unequal ion distribution is given either by the anion ratio X_A to Y_A or the cation ratio $(Z_M + Y_M)$ to X_M, which can be summarised as follows :-

For negative colloids $(M)_i > (M)_o$, $(A)_i < (A)_o$ and $pH_i < pH_o$

For positive colloids $(M)_i < (M)_o$, $(A)_i > (A)_o$ and $pH_i > pH_o$

The effect of the salt on the exchangeable cations will be to displace some of the hydrogen ions amongst other ions. The new equilibrium will result in a larger outside H activity X and a smaller inside activity (Y + Z).

Donnan equilibrium is the mass law applied to colloidal systems. Since the law of mass action demands that :-

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$

$$\frac{[H_2PO_4^-]_i}{[H_2PO_4^-]_o} = \frac{[H^+]_o}{[H^+]_i}$$

$H_2PO_4^-$ must have decreased as $\left[H^+\right]$ has increased and that their product must remain constant (Mattson and Barkoff 1953).

$$P_p \quad + \quad pH \quad = \quad \text{a constant}$$

$$P_p \quad = \quad - \log (H_2PO_4^-)$$

This constant has been called phosphoric potential (Aslying 1954).

3.1.5 The effect of electrolyte on the solubility of phosphate :-

The effect of electrolyte concentration on the solubility of phosphate has been studied by many workers. It has been found that dilute electrolyte solutions could depress the solubility of phosphate. (Mattson <u>et al</u> 1950; Clark and Peech 1960 and Lehr and Van Wesemael 1952). They demonstrated that in the case of salts with the same anion, the depressing effect on the solubility of soil phosphate increased in the order of the lyotropic series $Na < K < Mg < Ca$.

The effect was more pronounced at higher salt concentration. Sulphate has less depressing effects than chloride at higher concentration.

Solubility of phosphate may be different for pure phosphate from that of soil phosphate (Greaves 1910), due to the reaction between the soil and the salt solution.

However, it was found that the solubility of calcium phosphate in salt solution is more than in pure water (Mattson <u>et al</u> 1950), and the opposite is true with the sesquoxide-bound phosphate.

In a system containing both forms of phosphate and keeping the pH constant, the addition of salt gave the following effects:-

$$\text{Sesquoxide-bound P} \underset{\longrightarrow}{\xleftarrow{\text{salt}}} \text{calcium-bound P.}$$

On decreasing the pH the reaction was still the same as the above, while increasing the pH gave the opposite effect, i.e.

$$\text{Sesquoxide-bound P} \underset{\longleftarrow}{\xrightarrow{OH^-}} \text{Ca-bound P.}$$

The effect of the Donnan distribution was purely a valence effect, the more concentrated the salt, and the higher the valency of the cation, the thinner the double layer.

The order of the negative adsorption of anions was $SO_4 > Cl$. This effect is opposite to that of the cations which was $Na > K > Ca$. The difference with negatively adsorbed ions may be important in connection with the unequal ion distribution obtained on increasing the anion concentration.

At the same concentration the SO_4 ion gave rise to a greater $\frac{X}{Y}$ ratio than Cl ion, while with cations the effect of the degree of dissociation which varies with each cation follows the lyotropic series,

3.1.6 Chemical precipitation of phosphate:

The chemical precipitation of phosphates of varying composition depends on the predominant cations and on the specific surfaces formed by the mechanism of chemical precipitation which is related to the solubility product (Kittrick and Jackson 1955).

At low phosphate concentration the adsorption of phosphate by $CaCO_3$ can be described by the Langmuir isotherm (Cole et al 1953).

The adsorption of phosphate by soil was considered (Davis 1935 and Kurtz et al 1946) to be proportional to the concentration.

Phosphate adsorption by Ca-Kaolinite was found (Low and Black 1950, Russell and Low 1954) to fit the Freundlich equation and increase with temperature.

$$X = KC^{\frac{1}{P}}$$

X = the amount in unit weight of soil including that originally present.

C = The concentration of ion in the solution

K, P are constants.

From this it was concluded that the adsorption was a chemisorption and that the reaction was between the phosphate and the surface hydroxyl ions of the clay mineral.

However, the adsorption of phorphorus by soil from dilute solutions was found (Olsen and Watanabe 1957) to show a closer agreement with the Langmuir isotherm than with the Freundlich isotherm $\left(\frac{1}{K_m M} = \frac{Ceq}{X} - \frac{Ceq}{M}\right)$

where K_m = the equilibrium constant

Ceq = phosphate concentration in solution (μgmP/ml solution) at equilibrium

X = phosphate ion (μgmP/ml of solution) adsorbed by the surface.

M = maximum monolayer surface saturation (μgmP/ml of solution).

This was supported by Kuo and Lotse (1972) who found that the phosphate adsorption data fits the Langmuir isotherm.

This indicated that phosphate adsorption by $CaCO_3$ at low concentration forms a monolayer on the surface.

Adamson (1960) postulated the following principles from the Langmuir isotherm :-

(1) The energy of adsorption is constant (which implies uniform sites and no interaction between adsorbate molecules).

(2) The adsorption is on localized sites (which implies no translational motion of adsorbed molecules in the plane of the surface).

(3) The maximum adsorption possible corresponds to a complete monomolecular layer.

It seemed unlikely that all the three points above will hold for phosphorus in soil, i.e. the energy of phosphorus adsorption is likely to be constant only within a narrow concentration range. Also it seemed unlikely that adsorption will be restricted to a monolayer, particularly at higher concentrations, where some sort of lattice structure will begin to form.

Despite the above mentioned limitations (Larsen 1967), the Langmuir isotherm can often be used to give a relative measure of the energy by which phosphorus is bound to the solids (and a relative adsorption maximum). Based on this adsorption maximum and amount of readily isotopically exchangeable phosphorus already present in the soil, an arbitrary calculation of the degree of phosphorus saturation can be made. Such a measure has been shown to be related to plant uptake of soil phosphorus (Gunary and Sutton 1967).

It was summarised by Kuo and Lotse (1972) that the low activation energy of phosphate adsorption indicated that the adsorption is a diffusion controlled process. The diffusion of phosphate to the surface is dependent on the phosphorus concentration gradient between the bulk solution and the surface and the electrical potential difference between the surface and the ion (Kemper et al 1972).

It is well known that some of the phosphorus associated with the solid phase of soils which has been brought to equilibrium with phosphate solution is water soluble.

A distinction is frequently made between this phosphorus and the phosphorus ion more closely associated with the solid phase. Mattson and Karlesson (1938) have distinguished colloid-bond phosphate as ions that have become a diffusible structural unit in the colloidal aggregate and saloid-bound phosphate as ions in the diffusible ionic atmosphere held as compensation for ions of a positive charge.

These two forms of binding are different from extra miceller binding, which is precipitation of phosphate by another ion, when both are outside of the soil micelle .

(1) Crystal state:-

The chemical reaction product is sometimes a function of the cations present. For example, calcium is found to increase the fixation capacity of the soil for phosphorus (Allison 1943 and Ragland and Seay 1957).

It has been found also that calcium fluoride, as in the following equation can form calcium fluroapatite as considered by MacIntire and Hatcher (1942).

$$3\,Ca_3(PO_4)_2 + CaF_2 \longrightarrow Ca_{10}F_2(PO_4)_6$$

The phosphate ions removed from solution and passed to the solid phase may be added as a monolayer to a solid phase of the same kind (crystal growth), to a second solid phase (chemisorption) or else it may form new particles.

The insoluble phosphates of iron and aluminium will be precipitated in acid soil, and the insoluble phosphate of calcium and magnesium at pH values above 7.

The phosphate concentration in soil solution is governed by the solubility of calcium, aluminium and iron phosphates.

Phosphorus is most soluble in a system containing iron, aluminium and calcium at a pH near 7. At this pH most phosphorus is susceptible to translocation or utilisation and incorporation into the organic cycle.

At pH values below 7, the solubility of phosphorus is governed by iron and aluminium phosphates and decreases rapidly as the pH decreases.

At pH values above 7 phosphorus solubility is governed by calcium phosphates and decreases rapidly as the pH increases (Smeck 1973).

In a review of calcium compounds by Larsen (1967) it was concluded that only hydroxyl apatite was stable in a slightly acid range of soil condition.

Tricalcium phosphate can result from the precipitation of dicalcium phosphate as shown by the following equation :-

$$2CaHPO_4 + Ca^{2+} + 2HCO_3^- \rightleftharpoons Ca_3(PO_4)_2 + 2CO_2 + 2H_2O$$

The precipitation of the primary phosphate will take place by the action of calcium salts of weak acids as follows :- (Kugelmass and Rothwell 1924)

$$2NaH_2PO_4 + 3\ CaCO_3 \rightleftharpoons Ca_3(PO_4)_2 + Na_2CO_3 + 2H_2O + 2CO_2$$

While the secondary phosphate will be precipitated by the calcium salt of strong acids as follows :-

$$4Na_2HPO_4 + 3\ CaSO_4 \rightleftharpoons Ca_3(PO_4)_2 + 2NaH_2PO_4 + 3Na_2SO_4$$

Although the speed of chemical reactions generally increase with temperature (Hasman et al 1950) the extent to which this factor influences the fixation of soil phosphorus under field conditions is not well understood. It may be pointed out, however, that the soils of the warmer climates generally have more fixed phosphate than soils of more temperate regions (Mack and Barber 1960).

It should be remembered that these warmer climates give rise to soils with higher contents of hydrous oxides of aluminium and iron, which form a medium for phosphate adsorption. This can influence the availability of phosphorus to the plant.

(2) Amorphous state:-

In the amorphous state under waterlogged conditions iron is rapidly reduced from the ferric to ferrous state. This has an effect on phosphorus solubility. The hydrated iron oxide can crystallise in a variety of ways depending on the environment. (Oxidation reduction effect by altering the moisture content). Eriksson (1942) considered his findings on the effect of neutral salts on fixation of phosphates by amphoteric colloids in relation to the theory of Karlsson and Mattson (1940). This theory regarding repression of the hydrolysis of amphoteric phosphates by a salt supply can largely explain the reduction in phosphate solubility with potash addition.

The reduction in pH value will reduce or increase the more marked effect of the depression of hydrolysis, depending on whether the soil reaction is on the alkaline or acidic side of the solubility maximum.

This reduction of phosphate solubility with a supply of potash salt due to depression of the hydrolysis of the amphoteric soil colloids can probably be regarded as a normal phenomenon in ordinary surface soil, since the soil reaction in such soils is far above the isoelectric points of the soil complexes.

The changes in phosphate solubility arise from changes (due to the exchange acidity) in the pH value of the soil.

The difference in the effect between KCl and K_2SO_4 must be ascribed to the negative ions. $SO_4^{'}$ ions have a greater effect than Cl in counteracting the reduction in hydrolysis.

3.1.7 Extraction of soil phosphate:

Total and soluble phosphorus in different soils has been extracted by various extractants used for testing the effect of phosphate fertilizer on potatoes, swedes and grass in different British soils. Williams and Cooke (1962) examine the efficiency of these reactions and test phosphate availability as follows :-

(1) 0.3 M HCl 1:2.3 soil:solvent ratio, shaken for one min.

(2) 0.002 M H_2SO_4 1:200 soil:solvent ratio, shaken for 30 min.

(3) 0.5 M acetic acid 1:40 soil:solvent ratio, shaken for six hours.

(4) 0.1 M $CaCl_2$ solution 1:5 soil:water ratio, shaken at intervals.

(5) 1% citric acid 1:10 soil:solvent ratio, shaken for 24 hours.

(6) Acetic acid - sodium acetate buffer (HAc - NaAc), 1:5 soil:water ratio, shaken for 15 min.

(7) 0.5 M $NaHCO_3$ solution 1:20 soil: solution ratio, shaken for 30 min.

The extractants that differentiated best between responsive and unresponsive groups of experiments were HAc, HAc - NaAc and $NaHCO_3$ for potatoes and HCl, H_2SO_4, HAc - NaAc $NaHCO_3$ and $CaCl_2$ for grass.

It was concluded that under these experimental conditions, the best extractant was 0.5 M $NaHCO_3$. However, HCl, H_2SO_4 and the HAc - NaAc buffer solution methods were considered to be quite effective (Williams and Cooke 1962).

Soil phosphorus can be bound by Fe, Al and Ca depending on the pH of the soil, i.e. under acid conditions the binding agents are Fe and Al but Ca is the main binding agent under slightly acid to alkali conditions. However, the selective extractant (Williams 1970) for Al-bound P is NH_4F, for Fe-bound P is NaOH and for Ca-bound P is H_2SO_4.

Williams (1970) showed that for 40 Scottish soils, the lactate soluble phosphate was found to be highly correlated with the intensity values (see Section 3.1.3) as well as giving a good composite index of quantity and intensity.

0.5 M acetic acid of 1:5 soil:water ratio is now used by some advisory chemists in Scotland and England to extract phosphorus.

Lime and phosphate have been extracted using $CaCl_2$ solutions from 0.002 M – 0.05 M. Phosphate concentration in the filtrate was determined, then the activities were calculated. It was found that the lime potential was independent of calcium chloride concentration, but the phosphate potential of neutral and alkaline soils was decreased as the concentration of $CaCl_2$ was increased. However, if allowance was made for the formation of solid $CaHPO_4$ then the phosphate potential was also independent (Larsen 1965).

3.1.8 Ion uptake by plants:

The soil environment is an important factor which affects nutrient uptake by plants. In practical assessments of nutrient requirements consideration must be given to the micro-organisms and the plant itself. Nutrient uptake is closely related to the concentration or "potential" of inorganic ions in the soil solution, e.g. the metabolism of phosphate into nucleic acid and other compounds by bacteria can reduce the proportion of phosphate taken up by the roots.

Russell (1970) indicates that the mechanisms which operate when the external solution is dilute differ from that at higher concentration.

Higinbotham et al (1964), (1967) indicated that all anions (i.e. Cl, NO_3 , $H_2PO_4^-$ and SO_4) were actively transported into the cells of roots and coleoptiles of oats and roots and stems of peas.

Na, Ca, and Mg enter the cells by an energy-dependent process (i.e. accumulation ratio was in excess of one). They appear to be actively secreted. However, because of the low permeability coefficient of divalent cations they are probably excluded rather than actively secreted (Higinbotham et al 1967).

It was suggested (Hodges 1973) that variations in the field strength of binding sites on the ion carrier are responsible for the selectivity of ion absorption by roots. This selectivity of ion absorption by roots was considered (Hodges 1973) to be similar to the selectivity of ion binding to a glass electrode.

Hemwall (1957) mentioned that plant response to soil phosphorus is a function of the solubility of the phosphorus present and any factor which alters this solubility will alter the plant response.

In addition to effects of soil factors on phosphate solubility, plants can influence the solubility of soil phosphorus by some mechanism (Drake and Steckel 1955), i.e. the higher the cation exchange capacity of plant roots, the more effective is the plant at utilizing both applied rock phosphate and natural soil phosphorus.

The quantity of soluble phosphorus in the soil has an effect on the availability of phosphate to plants. The theory presented by Mattson _et al_ (1949) on the availability of phosphorus to plant is governed by the principle of the Donnan equilibrium.

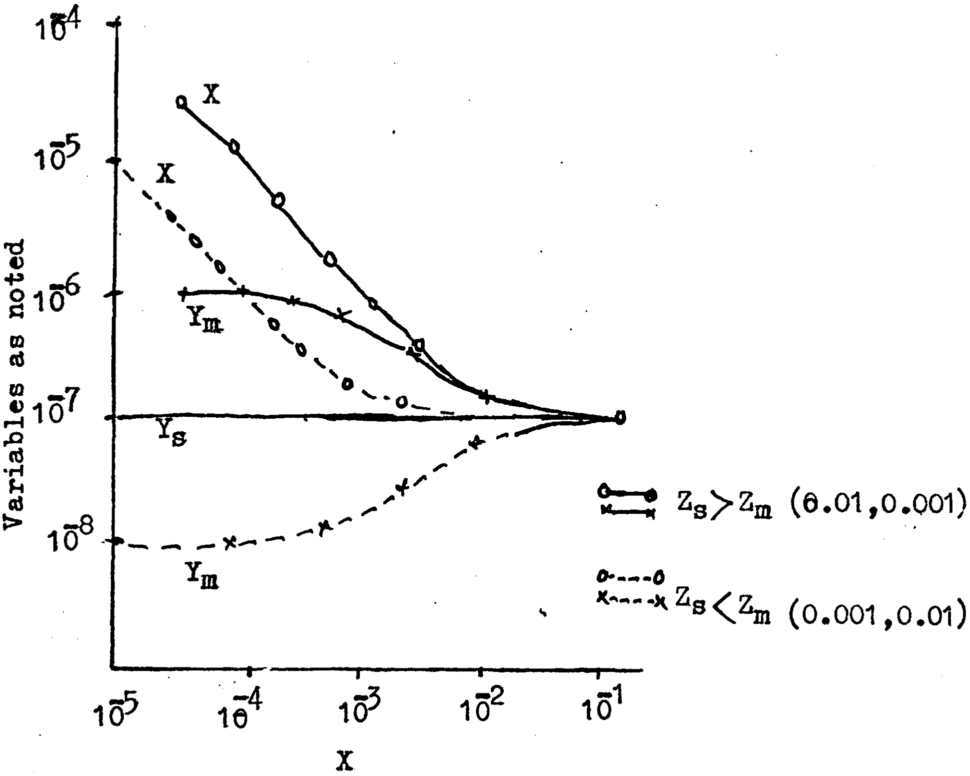
The range of the greatest salt effect on the suppression of Donnan distribution requires, for example, a higher salt concentration to produce the same effect on the anion uptake by peas as by rye, because the roots of the peas have a higher exchange capacity. The outer root membrane is readily permeable to all ordinary ions. This membrane fits closely on the inner protoplasmic membrane. The inner membrane is complicated in the mechanism of selection and active uptake of ions which is dependent on the physiology of the plant. It was concluded that the protoplasmic membrane depends directly on the content of the outer membrane and therefore only indirectly on the soil solution.

Assuming that only KH_2PO_4 was present, the presence of other salts suppress the Donnan distribution and eventually equilibriate the free ions of the system. In case of $Z_m > Z_s$ and $Y_m < Y_s$

s = soil

m = membrane

The addition of salt would promote the phosphate uptake because Y_m would get larger and approach the value of X which in turn would approach the practically unaffected constant value of Y_s. The salt effect would raise Y_m towards a maximum of four times more phosphate than that of the outside solution, as presented by Mattson in graphical form below.



A graphic representation of the theoretical distribution of ions between two colloidal phases. (Mattson et al 1950)

But when it is assumed that $Z_s > Z_m$ hence $Y_s < Y_m$, then the addition of salt would have the opposite effect and depress the phosphate uptake because Y_m would be reduced (by four times the base value for phosphate per unit volume) Y_s.

But when $Z_m = Z_s$ no effect of salt would occur.

It was concluded that the salt effect on the phosphate uptake by plants growing in a soil seem to depend, quantitatively as well as qualitatively on the relative activities of the soil and membrane acidoids. The uptake should be favoured by a low salt content if the cation exchange capacity of the soil is higher than that of the membrane, whereas a high salt content should favour the uptake if the exchange capacity of the root membrane is the higher.

It was found that with peas the uptake of the $H_2PO_4^-$ in 0.0025 N $CaCl_2$ was greater than in 0.0025 N KCl, and the latter solution was greater than in water. This was due to the ability of $CaCl_2$ to suppress the difference between X and Y_m more than KCl.

Mattson _et al_ (1949) concluded that the uptake of phosphate by plants was shown to be increased by the addition of neutral salt. This was due to a Donnan equilibrium phenomena, the phosphate diffusibility increases as its solubility decreases when salts are added.

Mattson _et al_ (1950) presented his theory of the availability of phosphorus to plants by postulating that an electrical double layer exists at the insoluble phosphorus soil solution interface, and at the soil solution plant root membrane interface, and that the distribution of ions between the interface, diffuse double layer, and solution is governed by the Donnan equilibrium principle.

The supply of cations should, however, be the minor problem in plant nutrition because the plant has two sources from which to draw the cations, those paired with anions and the cations obtained by exchange between the hydrogen ions of the root acidoid and the soil solutions.

Dean and Rubins (1945) and Islam (1956) showed that an equal phosphorus uptake took place from both the suspension and solution. This lead the authors to conclude that a mechanism of contact exchange (Jenney and Overstreat 1939) is not a factor in phosphorus nutrition of plants, or in other words it does not contribute to phosphate uptake. This could be related to the fact that there was no direct contact between the roots and the soil particles.

Plant absorption of exchangeable and soluble cations during periods of relatively low moisture content (range below field capacity and above the permanent wilting percentage) may turn salt diffusion to equilibrium in the soil system. Bear (1955) noted that diffusion is the movement of soluble salt upward or downward in the profile, also the exchange of cations in the interior of montmorillonite and interlayer mica K with cations in the solution is a diffusion reaction. However, Larsen (1967) defined diffusion as the transport or movement of molecules or ions where a difference in concentration exists in two parts of a system (liquid and solid phase), tending to move the system towards equilibrium.

Williams (1970) tried to relate the uptake of plant nutrients (especially P and K) to their quantity or intensity value or to the combination of both in the soil. While Mattingley et al (1963) found in his work that the uptake of phosphate by rye grass in the early stages of growth is closely related to the labile phosphate. (The following scheme was presnted by Williams (1970) for labile phosphate in soil solution and solid phase):-

$$\underset{\text{P-soil}}{\overset{\text{Slow}}{\text{Non-labile}}} \rightleftharpoons \underset{\text{P-soil}}{\overset{\text{Fast}}{\text{labile}}} \rightleftharpoons \text{P-solution} \xrightarrow{\text{movement}} \text{root surface}$$

The conclusion reached was that the mass flow contributed in bringing ions to the root surface.

Nye (1966) considered the operation of a single plant root as an absorbing cylindrical sink to which nutrients move by diffusion. The rate of nutrient uptake was assumed to be proportional to its concentration at the root surface.

Among soil properties, uptake should increase directly with the soil solution concentration. Uptake also increases (only slowly) with increasing buffering power and with increasing soil moisture. Among plant characteristics uptake increases with the root absorption power until diffusion through the soil becomes limiting.

Vaidyanathan and Nye (1966) summarised that the diffusion from soil of semi-infinite thickness is directly proportional to the square root of the diffusion time, until about half the counter ions originally on the resin have been exchanged by using ion exchange resin paper as a sink, and they also found that the effect of the counter ions of the resin on soil-ion flux in small but measurable.

3.2 METHODS

3.2.1 Preparation of solutions for measurement:

In general it was necessary to prepare three solutions namely :-

(1) The test solution made from the soil extract as in Section 3.2.2.

(2) A standard solution prepared from a known quantity of the substance to be estimated as described in Section 3.2.3.

(3) A blank solution containing all the reagents, but none of the substances.

3.2.2 Solution and Reagent:

(1) 1 ml was taken from filtrate

(2) 1.2 ml 60% perchloric acid

(3) 1 ml of 5% ammonium molybdate

(4) 0.5 ml of reducer reagent

(5) Volume was made up to 10 ml with the solvent which was used to extract the soil, i.e. either water or acetic acid. The sample was left for 10 minutes before measuring in an EEL colorimeter using filter 609.

Reagents:

(1) Perchloric acid 60%

(2) Ammonium molybdate 5%

(3) Reducing reagent.

0.5 gm 1 - amino - 2 napthol sulfonic acid, and 30 gm of $Na_2S_2O_5$ and 6 gm of Na_2SO_3 were individually weighed in separate weighing bottles. All of them were dissolved together in a 250 ml volumetric flask and then filtered and stored in a well sealed brown bottle. This solution was prepared each month.

3.2.3 Standards:

5.0332 gm NaH_2PO_4 were weighed directly into 1000 ml volumetric flask, using a weighing bottle, and the sample diluted to volume(stock A). 10 ml of stock solution (A) were diluted to 100 ml giving 100 ppm (Stock B).

Stock (B) was immediately transferred to a plastic bottle which had been rinsed with the solution.

Standards were prepared as follows :-

25 ml aliquot diluted to 50 ml volume giving 50 ppm standard
15 ml aliquot diluted to 50 ml volume giving 30 ppm standard
10 ml aliquot diluted to 50 ml volume giving 20 ppm standard
5 ml aliquot diluted to 50 ml volume giving 10 ppm standard

All these solutions were immediately transferred to plastic bottles.

A standard curve was drawn by plotting concentration against the optical density.

3.2.4 Effect of salt on P in soil:

A series of 100 ml samples of NaCl, Na_2SO_4, KCl, K_2SO_4, $MgCl_2$, $MgSO_4$, $CaCl_2$, $CaSO_4$, were taken from solutions containing 0, 2, 5, 10, 40, 60, 80 meq/l and were added to 10 gm air dry soil sample for both brown earth and gleyed soil, both top and sub soil batches. They were shaken on a rotary shaker for 16 hours before the soil suspensions were filtered through Whatman No 42 filter paper until absolutely clear. Then the soluble phosphate was measured.

3.2.5 Uptake of P by soil:

15.61 gm of NaH_2PO_4 was dissolved in one litre of two solvents, distilled water and acetic acid 0.5 N.

Then 0, 158, 415, 1550, 3100 mgP/100 ml solution were prepared by taking 0, 13, 50, 75, 100 of stock solution respectively and completing the volume to 100 ml. These were added to 10 gm air dry soil for brown earth top and sub soil. They were shaken on a rotary shaker for 16 hours at 18 - 21°C. The soil suspension was filtered through Whatman No 42 to give a clear extract and the P of this was measured colorimetrically.

3.2.6 Effect of salt on P with soil treated with 3.1 mgP/10 gm soil:

About 10 gm air dry soil samples for brown earth, top and sub soil were weighed out accurately. 1 ml from solution containing 310 mgP/100 ml was added to dry soil and it was left 7 hours before the addition of 100 ml of KCl solution taken from the solutions containing 0, 2, 5, 10, 40, 60, 80 meq/l. These were shaken on a rotary shaker for 16 hours at 18-21°C. Then the soil suspension was filtered through Whatman No 42 filter paper to give an absolutely clear extract. This was treated with 1:1.2 ratio of extract to 60% perchloric acid and left in a water bath for 30 minutes to oxidise the organic matter. Then the solution was centrifuged for 10 minutes to get rid of turbidity which absorbs and scatters light and causes error, before P was measured colorimetrically.

3.2.7 Effect of salt on P with soil treated with 40 mgP/10 gm soil:

10 gm air dry soil samples for brown earth, top and sub soil were weighed out accurately, then treated with 1 ml of NaH_2PO_4 salt solution containing 4000 mgP/100 ml (20.13 gm NaH_2PO_4/ 1000 ml). A volume of 100 ml distilled water containing weights of salt equivalent to a series of 0, 2, 5, 10, 40, 60, 80 meq/l for KCl, K_2SO_4, NaCl, Na_2SO_4, $MgCl_2$, $MgSO_4$, $CaCl_2$, $CaSO_4$ salts were added. The samples were shaken on a rotary shaker for 16 hours at 18-21°C. Then the soil suspensions were filtered through Whatman No 42 filter paper to give a clear solution. The extract was treated the same as in Section 3.2.8

by oxidising the organic matter, and the P of this solution was also measured colorimetrically.

3.3 RESULTS AND DISCUSSION

3.3.1 Uptake of P by soil:

Soils were found to have a high-adsorption capacity for phosphate in both solvents, acetic acid (0.5 M) and distilled water, when a series of different concentrations of NaH_2PO_4 from 158, 415, 1550, 3100 mgP/100 gm were added.

It was found that in the case of acetic acid the soil had a greater capacity to adsorb phosphate than from water, as shown in Table (3.1).

This may be related to the presence of iron and aluminium compounds (as noted by qualitative analysis) which increases the soil's ability to adsorb phosphate in acid media. This is supported by Mattson et al (1950).

With decreasing pH the reaction is as follows :-

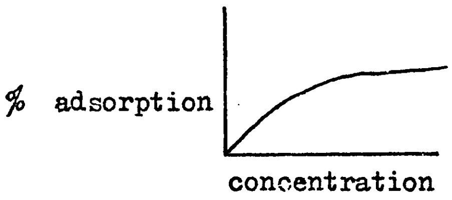
$$\text{Sesquioxide-bound P} \xrightleftharpoons{H^+} \text{Calcium-bound P}$$

Alternatively Williams and Saunders (1956) suggested the effect could be related to the breakdown of the octahedral layer with subsequent migration of partially hydrated aluminium ions to base exchange positions (Talibudeen 1957). These aluminium ions may be responsible for tying up phosphate.

Phosphate adsorption by soil was found to increase with increasing phosphate concentration. "The reason for this fact is not known" (Kuo and Lotse 1972).

At 415 mgP/100 gm it was found when distilled water was used as a solvent the soil adsorbed 25.9% to 30.0% phosphate, but with acetic acid as a solvent the soil adsorbed 31.8% to 43.2%.

At higher or lower concentrations than 415 gmP/100 gm the capacity of soil seemed to be less in both solvents. This may be related to the adsorption isotherms for phosphate (Barrow 1972).



In most cases the ability of sub soil to adsorb phosphate was found to be greater than for top soil. This may be due to the presence of greater amounts of organic matter in top soil than sub soil which reduces the effect of salt on the phosphate retention, or could be related to the higher amount of sesquioxides in the sub soil (Mattson <u>et al</u> 1950; Williams and Saunders 1956).

The ability of saline soil (gleyed soil) to take up phosphate was not investigated.

3.3.2 Effect of salt on P in soil:

The solubility of native phosphate was found to be decreased as the concentration of added salt was increased, as shown in Table (3.2), A, B, C, D.

This could be related to the Mattson <u>et al</u>(1950) theory :-

When the soil solution is diluted (control), there will be a Donnan redistribution of ions from the inside solution Y to the outside solution X or in other words Y decreases, but Y tends to be constant due to the equilibirum between the dissolved phosphate Y_P and the adsorbed phosphate S_P. Increase of the phosphate ratio must be caused by an increase of X_P

$$S_P \longrightarrow Y_P \longrightarrow X_P$$

In the presence of neutral salt the reaction goes in the opposite direction :-

$$S_P \longleftarrow Y_P \longleftarrow X_P$$

The salt induces phosphate adsorption and suppresses the solubility of phosphate.

Or this could be related to the replacement of calcium at the adsorptive complex by other cations. An excess of calcium (as common ion) in solution decreases the solubility of calcium phosphate (Lehr and Van Wesemael 1952).

In the case of the brown earth this decrease was found to be more than in gleyed soil. The range was $4.0 \times 10^{-5} - 9.0 \times 10^{-5}$ in brown earth soil, but in gleyed soil it was 0.2×10^{-5} - 6.5×10^{-5} except in the case of NaCl, it was 8.9×10^{-5}.

The difference in the reduced solubility of phosphate in brown soil which was higher than in gleyed soil could have been caused by the presence of a larger amount of calcium in brown soil than in gleyed soil, as shown in Table (2.11), or may be related to the increased formation of sesquioxide -bound P (Mattson et al 1950).

In brown soil the decrease in solubility of phosphate in the sub soil was more than in top soil. In the top soil the range was $4.0 \times 10^{-5} - 7.6 \times 10^{-5}$, but in the sub soil, $7.7 \times 10^{-5} - 9.0 \times 10^{-5}$, at 80 meq/l. This may be due to the presence of other compounds which decrease the solubility of phosphate. Their presence is suggested by the difference in percentage ignition between top and sub soil of brown earth, as shown in Table (2.3) (Doughty 1930, 1935).

In the gleyed soil the opposite was found. The range in the top soil was $0.4 \times 10^{-5} - 8.9 \times 10^{-5}$, but in sub soil it was $1.0 \times 10^{-5} - 4.4 \times 10^{-5}$, at 80 meq/l.

This change in solubility of phosphate may be related to the higher percentage of organic matter in the surface than in the sub soil which results in a reduction in the solubility of native phosphate (Burd 1948) , or could be related to a difference in CEC. A high value for Z means a greater difference between X and Y and a larger effect of salt on the X_p/Y_p ratio (Mattson et al 1950).

The effect of particular salts varied between the soil samples.

In the saline gleyed top soil, the addition of even higher concentrations of $MgSO_4$ and $CaCl_2$ (80 meq/l) resulted in only a slight decrease in the solubility of phosphate, as shown in Table (3.2 C) $0.2 \times 10^{-5} - 0.4 \times 10^{-5}$ mol P/1 respectively, while with the other soil samples the phosphate solubility remained in the same order, as shown in Table (3.2, A,B,D).

This could be due to the presence of high organic matter in gleyed soil which could adsorb calcium and magnesium ions, thereby becoming inactive to effect the solubility of phosphate. Thus the soluble phosphorus would be affected by the added salts, or the slight decrease could be due to the effect of calcium salts on the solubility which are inversely proportional to the concentration of $CaCl_2$ and $MgSO_4$ (Denman 1961, Longenecker and Lyerly 1959).

Increasing the chloride salts of Na and K decreased the phosphate solubility to a large extent in every case, as did the sulphates as shown in Table (3.2, A,B,C). These tables show that in the case of the sulphate of K a smaller reducing effect on the solubility of phosphate was noted than with chloride salt, except with gleyed sub soils. The Na salt of sulphate behaved similarly except in the case of brown earth top soil, where the opposite was true. For this reason, KCl was used for further experiments.

This reduction could be related to the difference in the effect of Cl and SO_4 salts on the thickness of the diffuse double layer, which decreases the solubility of phosphate by adsorption to the miceller atmosphere. Mattson explained this effect on the principle of Donnan equilibrium and more over the effect of the specific nature of the ions, (size, hydration, atomic weight, in addition to the valency).

This could be related to the effect of sodium and potassium salts on the solubility of calcium salts, i.e. the solubility of Ca salts is directly proportional to the concentration of sodium and magnesium chlorides (Denman 1961; Shternina 1957; Marshall and Slusher 1966; Nakayama and Rasnick 1967 and Longenecker and Lyerly 1959).

The Tables (3.2, A,B,D,C) show that the difference between the effects of the two K salts was greater in the top soil than in sub soil. It was 6.5×10^{-5} for KCl, 5.4×10^{-5} for K_2SO_4 in the gleyed top soil and 2.2×10^{-5} for KCl and 3.3×10^{-5} for K_2SO_4 in the gleyed sub soil. While in brown earth top soil it was 7.6×10^{-5} and 4.5×10^{-5} and in sub soil it was 8.3×10^{-5} and 7.7×10^{-5} for KCl and K_2SO_4 respectively as presented in Figs (3.1) and (3.2).

The difference between the effects of the two Na salts was almost exactly the same in top and sub soil of brown earth. It was 4.5×10^{-5} for NaCl, 4.8×10^{-5} for Na_2SO_4 in the brown earth top soil, 9.0×10^{-5} for NaCl and 8.3×10^{-5} for Na_2SO_4 in brown earth sub soil, as presented in Fig (3.1).

In the gleyed soil the difference was found to be greater in the case of the Na salt than for K salt, and greater in the top soil than in sub soil, as presented in Fig (3.2).

It was 8.9×10^{-5} for NaCl, 3.0×10^{-5} for Na_2SO_4; 6.5×10^{-5} for KCl and 5.4×10^{-5} for K_2SO_4 for top soil, while in the sub soil it was 4.4×10^{-5} for NaCl, 1.0×10^{-5} for Na_2SO_4,

2.2×10^{-5} for KCl and 3.3×10^{-5} for K_2SO_4.

Generally an increase in the chloride salt of Mg and Ca produced a slight decrease in the solubility of phosphate, but the sulphate salts produced an even smaller decrease, except in the case of brown earth top soil, where any sulphate salt used above, decreased the available phosphate more than the chloride salt; calcium salts in gleyed sub soil gave similar results.

It can be concluded from the above that on examining the effects of individual salts added, salts of monovalent anions appear to have a greater effect on decreasing the solubility of phosphate than salts of divalent anions, except in the case of brown earth top soil with Na and Mg salts and in gleyed soil with K salt.

3.3.3 **Effect of salt on P with soil** treated with 3.1 **mgP/10 gm soil:**

Phosphate was added to soil samples to study the effect of adding fertilizer, as shown in Tables (3.3) and (3.4).

The amount of phosphate added in one set of tests was equivalent to 400 mgP/100 gm soil, since subsidiary experiments showed that this dosage gave the greatest % phosphate retained in the soil; while in a second series a lower phosphate concentration, 31.0 mgP/100 gm soil was used to represent a more realistic level of available phosphate in soil for plants.

KCl, in varying concentrations was added to soil samples with the realistic phosphate dosage-31 mgP/100 gm soil. It was chosen because in the experiment on the effects of salts on native phosphate availability, it had given approximately similar results for the brown and gleyed soils.

Experiments were done with distilled water and with dilute acetic acid (0.5M) as solvents to study the effect of lower pH.

The solubility of phosphate when KCl salt was added in varying concentrations to the soil samples with a realistic phosphate dosage 31.0 mgP/100 gm soil, was found to depend on the media used.

For brown earth top soil the soluble phosphate was higher where acetic acid rather than water was used as the solvent in the absence of added KCl. This may be related to the presence of high amounts of calcium bound phosphorus which increases the solubility in acid condition. The opposite was true for sub soil as shown from the results in Table (3.3).

This was due to lowering of the pH to 4.5 which is more powerful for the extraction of insoluble phosphate than water. In top soil soluble phosphate was 4.4×10^{-4} mol P/l when acetic acid was used as solvent, but it was 2.4×10^{-4} mol P/l in distilled water.

In sub soil the figures were 1.8×10^{-4} and 3.2×10^{-4} respectively. This may be related to the increase in the formation of sesquioxide bound P which becomes more effective in this range of pH (Mattson et al 1950).

Both the gleyed sub soil and top soil were similar to the brown earth top soil. In top soil with acetic acid the solubility of phosphate was 4.0×10^{-4} mol P/1 but in water it was 2.2×10^{-4} mol P/1.
In sub soil with acetic acid it was 3.8×10^{-4} mol P/1 and in water 2.0×10^{-4} mol P/1. It was concluded that the soluble phosphate was greater in top soil than in sub soil.

But in brown earth soil it was found on extraction of soil by water that the sub soil had more soluble phosphate than top soil but when acetic acid was used as solvent, the top soil had more than sub soil, as shown in Table (3.3, A).

When KCl concentration was increased it tended to reduce the phosphate solubility in both media for top soil. In acetic acid it decreased from 4.4×10^{-4} to 1.0×10^{-4} mol. P/1 and in water from 2.4×10^{-4} to 0.8×10^{-4}. This explanation may be attributed to the Mattson theory :-

For a soil containing KCl, the $H_2PO_4^-$ - Cl equilibrium can be written

$$X_{H_2PO_4^-} / Y_{H_2PO_4^-} = X_{Cl} / Y_{Cl}$$

On dilution, Y_{Cl} decreases faster than X_{Cl} and the ratio therefore increases $X^2 = Y(Y + Z)$. As long as $Y_{H_2PO_4^-}$ is constant, the corresponding increase of the phosphate ratio must be caused by an increase of ${}^{X}H_2PO_4^-$. This means that the progressive addition of water to the soil increases the concentration of phosphate in solution until ${}^{Y}H_2PO_4^-$ is no longer constant. The adsorption of phosphate is :-

$$S_P \longrightarrow Y_P \longrightarrow X_P$$

but with addition of salt the reaction of adsorption of phosphate is reversed

$$S_P \longleftarrow Y_P \longleftarrow X_P$$

While in acid media the adsorption of phosphate was related to this equation as follows :-

$$\text{Sesquioxide bound P} \xrightleftharpoons[\text{or acid media}]{\text{Salt}} \text{Ca-bound P}$$

KCl increased the phosphate solubility in both media for the sub soil. The experiment was done in duplicate, also the results are the mean of three readings in an attempt to eliminate errors due to the inhomogeneous nature of the soil samples.

In water from 3.2×10^{-4} to 6.7×10^{-4}, while in acetic acid from 1.8×10^{-4} to 5.0×10^{-4} mol P/l.

Under similar concentrations of KCl it was found that phosphate solubility was reduced in both media for top and sub soil of gleyed soil.

In both media for top soil it was decreased from 4.0×10^{-4} to

0.9×10^{-4} with acetic acid and in water from 2.2×10^{-4} to 0.8×10^{-4}, while in sub soil it decreased from 2.0×10^{-4} to 0.7×10^{-4} for water, and 3.8×10^{-4} to 0.8×10^{-4} with acetic acid.

In addition, as KCl increased the solubility of phosphate in each solvent, the phenomenon could be explained by sesquioxide present in brown earth sub soil, as noted by qualitative analysis. The presence of sesquioxide appears to reduce the amount of phosphate more in acid media. When salt was added the ability of sesquioxide to adsorb phosphate was decreased, and the solubility of phosphate started to increase.

3.3.4 Effect of salt on P with soil treated with 40 mgP/10 gm soil:

When high concentrations of phosphate were added (400 mgP/100 gm soil) to soil, the effect of different types of salt was investigated.

The different types of salt were all found to decrease the solubility of phosphate, as shown in Table (3.4, A,B).

It was found that Cl salt had a slightly greater effect than the SO_4, as found in the experiments on native phosphate.

The order of decreasing the solubility of added phosphate (Fig. 3) was :-

Cl salt at 10 meq/l top soil and sub soil respectively:-

Ca > Mg > K > Na
3.0 > 2.1 > 1.5 > 1.1 (Top soil)
2.2 > 2.0 > 1.9 > 1.7 (Sub soil)

SO_4 salt at 10 meq/l top soil and sub soil respectively :-

$$\begin{array}{lllll} Ca & > Mg & > K & > Na & \\ 2.0 & > 1.4 & > 0.9 & > 0.7 & \text{(Top soil)} \\ 2.2 & > 1.7 & > 1.6 & > 1.5 & \text{(Sub soil)} \end{array}$$

The order in which cations were found to decrease the solubility of phosphate was the same as the lyotropic series.

Mattson suggests that the ability of the ion to gather an atmosphere of water molecules reduces its ability to diffuse through the double layer depressing the potential difference and thereby lowering the phosphate solubility, or in other words the activity of ions was reduced, (valid for monovalent series), or may be related to the solubility product of the phosphate salt.

For native phosphate most chlorides decreased the solubility of phosphate more than sulphates. This trend is slight for added phosphate. This may be because the processes by which the phosphate enters solution are different in the two cases, or may be related to the difference in concentrations of phosphate.

The presence of salts in soil may have an important effect on uptake of phosphate by plants. The plant soil relationship however was not investigated.

Mattson <u>et</u> <u>al</u> (1949) found that neutral salts increase the uptake of phosphate ionsby plant. This effect is explained on the basis of the Donnan distribution of the ions. This theory was firstly tested on a simple cellophane membrane. It was found that the addition of salts caused a more rapid diffusion of ions through the cellophane membranes. The amount of phosphate diffused through the membrane was found to agree with both the lyotropic effect and valence effect ($Na < K < Mg < Ca$).

Mattson et al (1949) noted that the diffusion of phosphate acid is considered to be a function of pH ($H_3PO_4 > H_2PO_4^- > HPO_4^{=}$).

There is no doubt, applying the theory mentioned above to the living root membrane as well as to the cellophane membrane, the uptake of phosphate ions is affected by the salt concentration.

However the uptake of ions by plants depends on the nature of the soil exchange complex with which the root acidoids have to compete.

Table (3.1)

The capacity of soil to retain phosphate

Added mgP/100 gm	Brown earth top soil % retained		Brown earth sub soil % retained	
	H_2O	Acetic acid	H_2O	Acetic acid
3100	7.5	25.8	9.7	24.7
1550	9.8	25.8	16.5	32.1
415	25.9	31.8	30.0	43.2
158	10.8	27.6	8.6	26.1

Results are the mean of the two soil samples and are measured in triplicate.

Table (3.2)

The effect of salt on the solubility of native phosphate

A - Brown earth top soil

Conc. meq/l	$\times 10^{-5}$ molP/l							
	NaCl	Na_2SO_4	KCl	K_2SO_4	$MgCl_2$	$MgSO_4$	$CaCl_2$	$CaSO_4$
0	10.9	10.9	10.9	10.9	10.9	10.9	10.9	10.9
2	7.7	7.7	5.5	7.7	7.7	7.6	7.6	7.7
5	7.8	7.7	5.1	7.8	7.5	7.4	7.4	7.4
10	7.7	7.1	4.0	7.1	7.4	7.4	6.9	6.5
40	6.6	6.5	3.8	6.6	7.4	6.8	6.8	nd
60	6.5	6.3	3.3	6.5	7.3	6.8	6.6	nd
80	6.4	6.1	3.3	6.4	6.9	6.5	6.5	nd
0–80	4.5	4.8	7.6	4.5	4.0	4.4	4.4	

B - Brown earth sub soil

Conc. meq/l	$\times 10^{-5}$ molP/l							
	NaCl	Na_2SO_4	KCl	K_2SO_4	$MgCl_2$	$MgSO_4$	$CaCl_2$	$CaSO_4$
0	12.2	12.2	12.2	12.2	12.2	12.2	12.2	12.2
2	12.2	8.8	8.8	8.9	8.7	9.0	8.3	8.5
5	6.7	7.1	8.1	8.5	7.8	8.1	7.7	7.8
10	6.7	6.8	7.1	7.5	6.8	7.1	7.1	7.7
40	4.4	6.0	6.1	6.4	5.2	5.9	6.1	nd
60	3.3	5.2	4.1	4.4	3.6	4.1	3.7	nd
80	3.2	3.9	3.9	4.5	3.8	4.2	3.8	nd
0–80	9.0	8.3	8.3	7.7	8.4	8.0	8.4	nd

nd = not determined

Results are the m~~ai~~ean of the two soil samples and measured in triplicate.

Table (3.2)

The effect of salt on the solubility of native phosphate

C – Gleyed top soil

Conc. meq/l	x 10^{-5} molP/l							
	NaCl	Na_2SO_4	KCl	K_2SO_4	$MgCl_2$	$MgSO_4$	$CaCl_2$	$CaSO_4$
0	9.8	9.8	9.8	9.8	9.8	9.8	9.8	9.8
2	9.8	9.8	9.7	9.8	9.8	9.7	9.7	9.7
5	6.5	7.4	6.7	8.7	9.4	9.7	9.3	9.4
10	5.4	7.4	6.6	7.6	9.4	9.7	9.2	9.3
40	4.2	6.8	7.1	4.4	8.1	9.6	9.0	nd
60	3.3	6.8	3.3	4.4	7.1	9.6	9.0	nd
80	0.9	6.8	3.3	4.4	6.5	9.6	9.4	nd
0–80	8.9	3.0	6.5	5.4	3.3	0.2	0.4	–

D – Gleyed sub soil

Conc. meq/l	x 10^{-5} molP/l							
	NaCl	Na_2SO_4	KCl	K_2SO_4	$MgCl_2$	$MgSO_4$	$CaCl_2$	$CaSO_4$
0	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7
2	7.7	7.7	6.6	7.7	7.7	7.7	8.9	7.1
5	6.7	7.4	6.6	5.5	6.5	6.5	7.7	7.1
10	6.7	7.2	5.5	4.4	6.5	6.5	6.9	6.8
40	6.6	7.2	5.5	4.4	5.0	6.5	6.7	nd
60	5.5	6.7	5.5	4.4	4.9	6.5	3.5	nd
80	3.3	6.7	5.5	4.4	4.8	6.1	3.5	nd
0–80	4.4	1.0	2.2	3.3	2.9	1.6	4.2	–

nd = not determined

Results are the mean of the two soil samples
and measured in triplicate

Table (3.3)

The effect of KCl salt on the solubility of added phosphate

31 mgP/100 gm soil was added.

A – Brown earth soil

Conc. meq/l	Brown earth top soil		Brown earth sub soil	
			$\times 10^{-4}$ mol P/l	
	H_2O	Acetic acid	H_2O	Acetic acid
0	2.4	4.4	3.2	1.8
2	2.6	3.3	3.2	1.4
5	1.9	2.4	3.3	1.1
10	1.3	1.0	3.2	1.5
40	0.9	1.3	3.1	2.5
60	0.9	1.3	5.0	5.1
80	0.8	1.0	6.7	5.0
0–80	1.6	3.4	– 3.5	– 3.2

B – Gleyed soil

Conc. meq/l	Gleyed top soil		Gleyed sub soil	
			$\times 10^{-4}$ mol P/l	
	H_2O	Acetic acid	H_2O	Acetic acid
0	2.2	4.0	2.0	3.8
2	2.0	3.8	1.8	3.5
5	1.6	2.5	1.3	3.2
10	1.2	2.0	1.1	2.0
40	0.9	2.5	0.9	2.2
60	0.8	1.5	0.8	1.8
80	0.8	0.9	0.7	0.8
0–80	1.4	3.1	1.3	3.0

Results are the mean of two soil samples and measured in triplicate.

Table (3.4)

The effect of salt on the solubility of added phosphate

400 mgP/100 gm soil.

A - Brown earth top soil

Conc. meq/100 ml	$\times 10^{-3}$ molP/l							
	NaCl	Na_2SO_4	KCl	K_2SO_4	$MgCl_2$	$MgSO_4$	$CaCl_2$	$CaSO_4$
0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0
2	7.7	7.8	6.7	7.8	6.8	7.2	6.0	6.6
5	6.9	7.7	6.7	7.5	6.5	6.8	5.2	6.4
10	6.9	7.4	6.5	7.1	5.9	6.6	5.0	6.0
40	6.4	7.0	6.4	6.6	5.6	6.3	4.8	nd
60	6.3	6.4	6.0	6.1	5.4	6.0	4.6	nd
80	nd	nd	nd	nd	nd	nd	nd	nd
0–10	1.1	0.7	1.5	0.9	2.1	1.4	3.0	2.0

B - Brown earth sub soil

Conc. meq/100 ml	$\times 10^{-3}$ molP/l							
	NaCl	Na_2SO_4	KCl	K_2SO_4	$MgCl_2$	$MgSO_4$	$CaCl_2$	$CaSO_4$
0	8.3	8.3	8.3	8.3	8.3	8.3	8.3	8.3
2	8.1	8.2	7.5	8.0	7.5	8.2	7.3	7.4
5	6.7	6.8	7.2	6.8	7.4	7.8	6.4	6.4
10	6.6	6.8	6.2	6.7	6.3	6.6	6.1	6.1
40	6.5	6.8	6.1	6.5	5.1	6.4	5.3	nd
60	6.4	6.7	6.1	6.5	5.8	6.1	5.2	nd
80	6.4	6.7	6.1	6.5	5.8	5.8	5.2	nd
0–10	1.7	1.5	1.9	1.6	2.0	1.7	2.2	2.2

nd = not determined

Results are the mean of two soil samples and measured in triplicate.

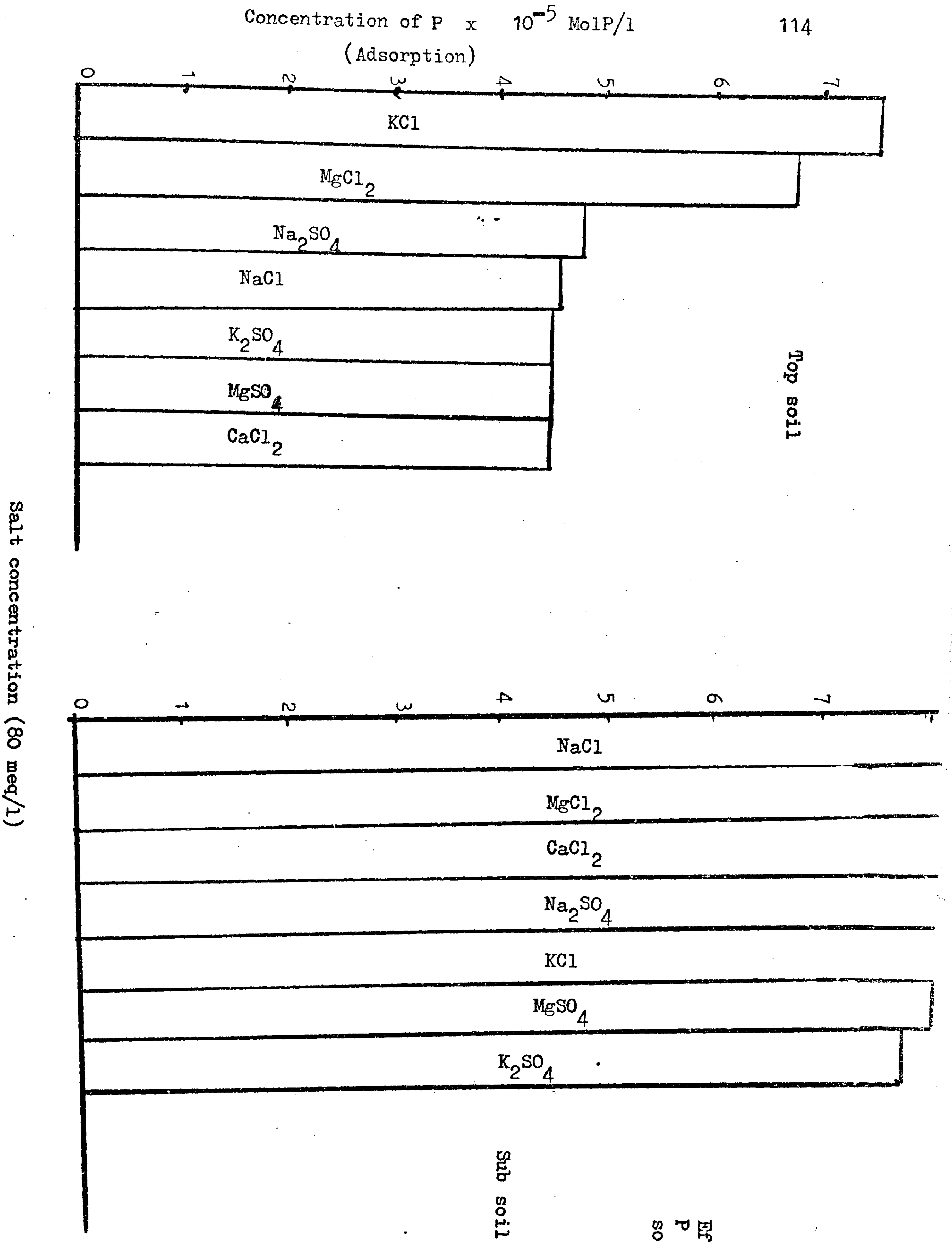


Fig. 3.1
Effect of salt on P in brown earth soil.

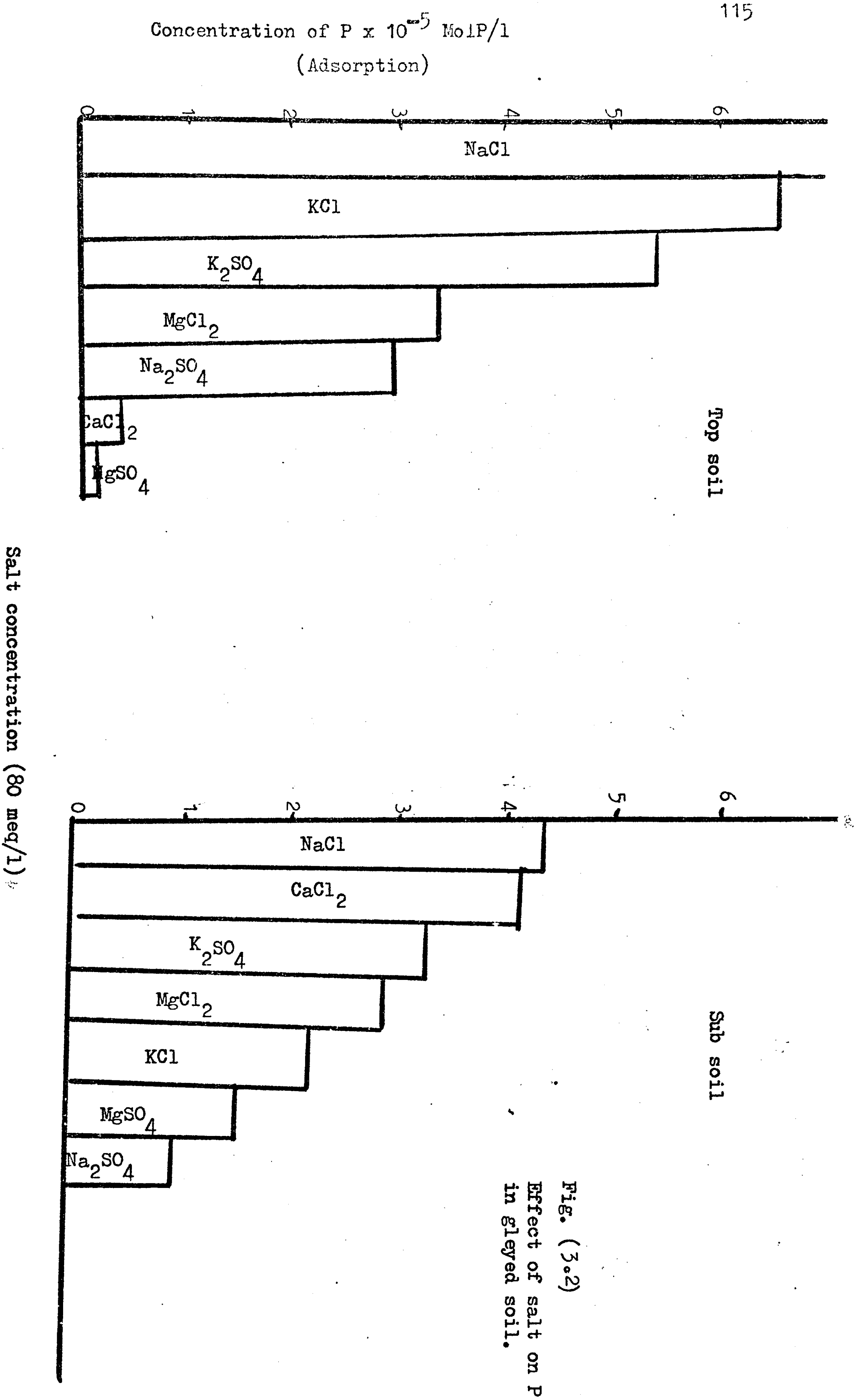


Fig. (3.2)
Effect of salt on P
in gleyed soil.

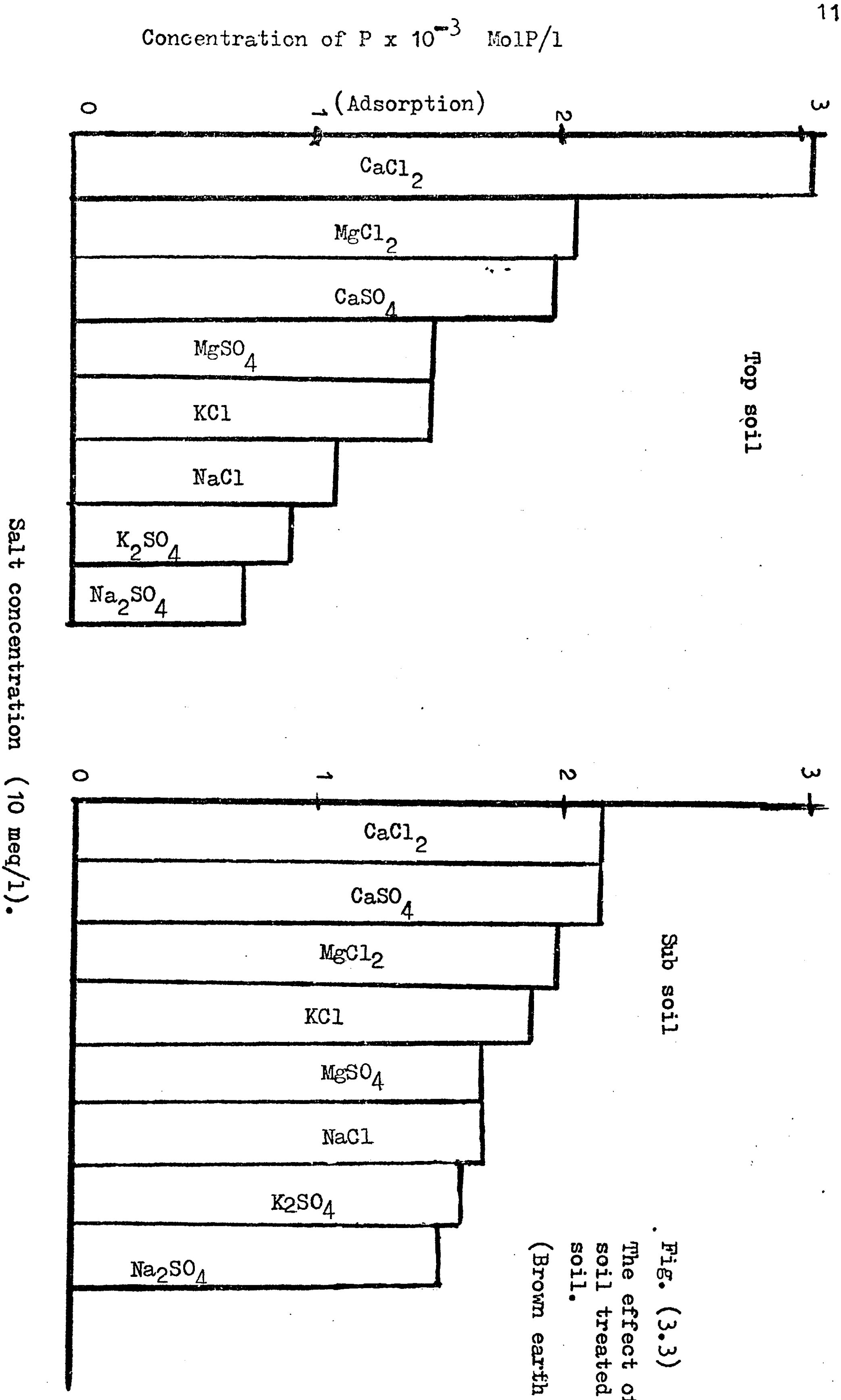


Fig. (3.3)
The effect of salt on P with soil treated with 40 mgP/10 gm soil.
(Brown earth soil)

CHAPTER FOUR

THE EFFECT OF SALT ON THE DISSOCIATION OF $CaCO_3$

4.1 INTRODUCTION

The solubility of $CaCO_3$ is controlled by the pH. The pH is dependent on the amount of CO_2 present. The concentration of CO_2 in the atmosphere is 0.03% while it is up to 4% in wet, warm soils when it reaches toxic levels.

This increase in the concentration of CO_2 may be related to the activity of micro-organisms and respiration of root systems, which is very important to the plant growth.

The pH value of distilled water is about 5.7. This is related to the contact of water with the CO_2 from atmosphere which reduces the pH value from neutral to slightly acid, as expressed by the equations:-

The pH of pure water in equilibrium with atmosphere -

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

$$pK = \frac{[H_2CO_3]}{P_{CO_2}}$$

$$= 10^{-1.5}$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$pK = \frac{[H^+]\ [HCO_3^-]}{[H_2CO_3]}$$

$$= 10^{-6.4}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^=$$

$$pK = \frac{[H^+]\ [CO_3^=]}{[HCO_3^-]}$$

$$= 10^{-3.5}$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K_{H_2O} = \frac{[H^+]\ [OH^-]}{[H_2O]}$$

$$= 10^{-14}$$

$$H_2CO_3^- = 10^{-1.5}\ P_{CO_2}$$

When $P_{CO_2} = 10^{-3.5}$ atmosphere

$$[H^+] = [OH^-]$$

$$[H^+]^2 = 10^{-6.4} \times 10^{-1.5} \times 10^{-3.5}$$

$$= 10^{-11.4}$$

$$pH = 5.7$$

The activity of $CO_3^=$ however, is reduced by the complex forming ability of CO_3 (Sverdrup 1942). In addition Ca and Mg interact with CO_3 and HCO_3 to form soluble complexes (Greenwald 1941). The existing equilibrium at 22°C when the ionic strength of the solution is equal to 0.15 is as follows :-

$$K'_{CaHCO_3^+} = \frac{m_{Ca^{2+}}\ m_{HCO_3^-}}{m_{CaHCO_3^+}}$$

$$= 1.6 \times 10^{-1}$$

$$K'_{MgHCO_3^+} = \frac{m_{Mg^{2+}} \; m_{HCO_3^-}}{m_{MgHCO_3^+}}$$

$$= 1.7 \times 10^{-1}$$

$$K'_{CaCO_3^o} = \frac{m_{Ca^{2+}} \; m_{CO_3^=}}{m_{CaCO_3^o}}$$

$$= 1 \times 10^{-3}$$

$$K'_{MgCO_3^o} = \frac{m_{Mg^{2+}} \; m_{CO_3^=}}{m_{MgCO_3^o}}$$

$$= 4.3 \times 10^{-3}$$

It has been stated (Harvey 1957) that neutral salts greatly increase the solubility of calcite.

Most of the complexing of major dissolved species and important aspects of complexing of minor species can be related to the formation of ion pairs in solution. Ion pairs can be explained on the basis of a deficiency of free ions in solution, due to the short range interactions between closely adjacent ions usually in pairs (covalent bond). The equilibrium constant can be expressed as association constant, or the reciprocal of this.

The dissociation constant (the proportion of undissociated salt in the solution) for some dissolved species in aqueous solution at 25°C is as shown in Table (4.5).

The mass action expression is constant only in dilute solutions, while in more concentrated solutions interionic attraction must be considered because of their ability to form complexes.

The dissociation of water can be represented as :-

$$H_2O \rightleftharpoons H^+ + OH^-$$

Each of the ions is hydrated to :-

$$H\,\underset{H}{:\ddot{\underset{..}{O}}:} + H\,\underset{H}{:\ddot{\underset{..}{O}}} \rightleftharpoons H\,\underset{H}{:\ddot{\underset{..}{O}}:}\,H^+ + :\ddot{\underset{..}{O}}:\,H^-$$

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

However, the degree of dissociation of water is very small. In pure water the concentration of hydrogen ions is 1×10^{-7}M and the concentration of OH ions is the same.

The free ions in equilibrium with the ion pairs in solution of a given ionic strength will have ion activity coefficients appropriate to their particular ionic strength. These activity coefficients could be calculated(for dilute solution only) from the Debye-Huckel theory (1923) :-

$$PF_i = -\log fi = \frac{AZ_i^{\,2}\sqrt{I}}{1 + B\,di\sqrt{I}}$$

A = constant for water dependent on the temperature

B = constant dependent on the value of di (ionic diameter)

Z_i = valency

I = ionic strength ($I = \frac{1}{2}\sum M_i\ Z_i^{\,2}$)

M_i = concentration (in moles)

For single ionic species the contribution of ions to the ionic strength is :-

Uni-univalent	1:1	valent	electrolyte	e.g. NaCl, KCl I = M
Uni-bivalent	1:2	"	"	e.g. $MgCl_2$, $CaCl_2$ I = 3M
Bi-bivalent	2:2	"	"	e.g. $MgSO_4$, $CaSO_4$ I = 4M

The dissociation of the cations depends not only upon valency but also upon other factors, amongst which are atomic volume and the degree of hydration of the ions.

The smaller the volume of the cation the greater the hydration, i.e. the greater the number of water molecules attached to the ions, which reduces its effective electrostatic charge.

The higher the valency and the lower the hydration the more easily the ion is attracted to the opposite sign of charge round another ion (Eigen and Wicke 1954).

The ions move in a random manner. If one focussed attention on one ion, that ion would be surrounded more by oppositely charged ions than by like charges. An ion has therefore an oppositely charged ion atmosphere. The ion atmosphere around each ion is, of course, better formed at higher concentrations. However, higher concentrations are not dealt with by the Debye-Huckel theory, but it is often directed to the formation of ion pairs.

It was concluded (Garrels and Christ 1965) that the pK value for ion pairs is independent of cation size and in fact all divalent $MeSO_4^o$ ion pairs in solution have nearly the same pK = 2.3.

Similarly, all monovalent $MeSO_4^-$ pairs also have about the same pK = 0.8

None of the major cations of natural water seem to interact significantly with chloride ionsto form ion pairs. This interaction can occur with Na, Ca, Mg with each of the anions $SO_4^=$, HCO_3^- and $CO_3^=$ while K interacts only with $SO_4^=$.

Tentatively then the important dissolved species in sea water may include K^+, KSO_4^- Na^+ $NaCO_3^-$, $NaHCO_3^o$, $NaSO_4^-$ Ca^{2+}, $CaHCO_3^+$, $CaCO_3^o$, $CaSO_4^o$, Mg^{2+}, $MgHCO_3^+$, $MgCO_3^o$, $MgSO_4^o$, HCO_3^-, $CO_3^=$, $SO_4^=$ and Cl^- (Garrels and Christ 1965).

The activity coefficients for various species in sea water (charged and uncharged) at 0.7 ionic strength are shown in Table (4.7).

The analytical value given for $SO_4^=$ which can be designated $MSO_4^=$ total, can be equated to the sum of the various species containing sulphate as follows :-

$$^{m}SO_4^= \text{ total} = {}^{m}SO_4^- + {}^{m}KSO_4^- + {}^{m}CaSO_4^o + {}^{m}MgSO_4^o + {}^{m}SO_4^= \text{ free}$$

For a fixed activity of water, the activity of $CaSO_4^o$ is also fixed, and any increase in the $SO_4^=$ content of sea water (by evaporation) will increase the fraction of these ion pairs present as $CaSO_4^o$ or $MgSO_4^o$.

Gypsum begins to precipitate at equilibrium from concentrated sea water as follows :-

$$CaSO_4 \cdot 2H_2O_C = CaSO_4^o{}_{aq} + 2H_2O_L$$

$$\left[CaSO_4^o\right]\left[H_2O\right]^2 = K_{gypsum}$$

$$CaSO_4^o{}_{aq} = Ca^{++}{}_{aq} + SO_4^={}_{aq}$$

$$K_{CaSO_4^o} = \frac{\left[Ca^{++}\right]\left[SO_4^=\right]}{\left[CaSO_4^o\right]}$$

where L = liquid

The chemical model of sea water is presented in terms of the anions $SO_4^=$, HCO_3^- and $CO_3^=$.

More than 30% of $SO_4^=$ and HCO_3^- is tied up as ion pairs, with cations, whereas 90% of the total $CO_3^=$ is complexed.

From Table (4.5) it is clear that the dissociation constant for Na salts is more than Mg salts. Thus Mg salts produce more ionic pairs than Na salts (see Garrles and Christ 1965), Table (4.6).

The relatively high stability of the $MgCO_3^o$ ion pairs indicates that Mg exerts an important indirect control on $CaCO_3$ solubility which results in a major redistribution of CO_2 between the atmosphere and the ocean.

The equilibrium constant for $CaCO_3$ as presented (Garrles and Christ 1965) at 25°C is as follows :-

$$K_{CaCO_3} = \frac{[Ca^{2+}]\,[CO_3^{=}]}{[CaCO_{3_C}]}$$

$$= 10^{-8.3}$$

$$K_{H_2CO_3} = \frac{[H^+]\,[HCO_3^-]}{[H_2CO_3]}$$

$$= 10^{-6.4}$$

$$K_{HCO_3^-} = \frac{[H^+]\,[CO_3^{=}]}{[HCO_3^-]}$$

$$= 10^{-10.3}$$

$$K_{CO_2} = \frac{[H_2CO_3]}{P_{CO_2\ g}}$$

$$= 10^{-1.47}$$

4.2 METHODS

4.2.1 Preparation of solutions for measurement:

25 ml of extract were taken and put in a conical flask. A few drops of phenolphthalein solution were added, and the liquid titrated with standard H_2SO_4 until the pink colour disappeared, then three drops of methyl orange solution were added and the titration was continued until the indicator turned red. The volume of acid used was recorded; the titration was repeated with distilled water.

4.2.2 Reagents:

Phenolphthalein: 0.5 gm phenolphthalein indicator was dissolved in 50 ml of alcohol and 50 ml H_2O were added.

Standardization of H_2SO_4:

It was titrated against standard NaOH to find its exact concentration.

4.2.3 Effect of salts (NaCl, $MgCl_2$) on the solubility of $CaCO_3$ in distilled water (equilibrium with atmospheric CO_2)

0.1 gm $CaCO_3$ was weighed accurately and added to a series of 100 ml of 0, 2, 5, 10, 40, 60, 80, 100 meq/l of NaCl, $MgCl_2$, and a mixture of $MgCl_2$ + NaCl was also added. This was done also with 1.0 gm $CaCO_3$.

The samples were shaken on a rotary shaker for 18 hours at 17.5°C; the pH of the suspension was then measured. Suspensions were filtered through Whatman No 42 filter paper to give a clear solution. The Ca of this solution was measured by atomic absorption.

4.2.4 Effect of sulphate and chloride salts of Na, K and Mg on the solubility of $CaCO_3$ by shaking with soil treated with 1 gm $CaCO_3$:

10 gm each of top and sub soil samples of brown earth were treated with 1 gm of powdered $CaCO_3$.

A volume of 100 ml distilled water containing weights of salts equivalent to a series of 0, 10, 40 meq/l of NaCl, Na_2SO_4, KCl, K_2SO_4, MgCl and $MgSO_4$ salt were added.

These samples were shaken on a rotary shaker for 16 hours at 18 - 21°C, then the soil suspensions were filtered through Whatman No 42 filter paper. The concentrations of Ca, Na, K, Ca and Mg in these solutions were measured.

4.2.5 Effect of NaCl, $MgCl_2$ and NaCl + $MgCl_2$ salts on the solubility of $CaCO_3$ by leaching with soil treated with 1 gm $CaCO_3$:

1 gm of $CaCO_3$ powder was weighed out accurately and added to a mixture of 10 gm soil samples with 10 gm acid washed sand. The constituents were added to four columns and were prepared as above. Then the columns were washed with 4 x 100 ml of H_2O, 1000 meq/l NaCl, 1000 meq/l $MgCl_2$ and (500 meq/l NaCl + 500 meq/l $MgCl_2$) respectively, and 100 ml of the leachate of each was collected separately. Each column was then left with 100 ml solution for 18 hours at 17 - 20°C and the leachate collected. Ca for all these aliquots was measured.

4.2.6 Effect of salts (NaCl, $MgCl_2$ and NaCl + $MgCl_2$) on the solubility of $CaCO_3$ by shaking with soil treated with 1 gm $CaCO_3$:

1.0 gm of $CaCO_3$ powder was weighed out accurately and added to 10 gm soil sample. Then 100 ml of H_2O, 1000 meq/l NaCl, 1000 meq/l $MgCl_2$ and (500 meq/l NaCl + 500 meq/l $MgCl_2$) were added individually. They were shaken on a rotary shaker for 16 hours at 17°C. The pH of each suspension was then measured. The soil suspensions were filtered through Whatman No 42 filter paper to give a clear solution. Ca concentrations of these solutions were measured.

4.3 RESULTS AND DISCUSSION

4.3.1 Effect of NaCl and $MgCl_2$ salts on the solubility of calcium ions in water in equilibrium with CO_2 in the atmosphere:

In the absence or presence of salts the mobility of Ca in solution was not proportional to the concentration of $CaCO_3$. It was found that in the absence of salt, the mobilization of calcium was greater in total but lower in % terms in the solution with the higher concentration of $CaCO_3$ than in the solution with the low concentration of $CaCO_3$ as shown in Table (4.1). The figure was 0.3 meq Ca/100 ml mobilized in the presence of 0.1 gm $CaCO_3$ while 0.5 meq Ca/100 ml in the presence of 1.0 gm $CaCO_3$. This could be related to the surface area effect in increasing the mobilization of calcium from $CaCO_3$ in dilute solution.

The ability of salts to liberate calcium ions was found to increase as their concentrations increased, but not proportional to the concentrations as shown in Table (4.1).

In the solution with higher concentrations of $CaCO_3$ (1.0 gm) the increase in the solubility of calcium was slightly more than in the solution containing lower concentrations (0.1 gm $CaCO_3$/ 100 ml for both types of salt added).

In the solution containing lower concentrations of $CaCO_3$ this effect was noticed up to 0.6 meq Ca/100 ml for NaCl and up to 1.2 meq Ca/100 ml for $MgCl_2$. Thus in the solution containing higher concentration up to 0.9 meq Ca/100 ml for NaCl up to 1.3 meq Ca/100 ml for $MgCl_2$ was noted, as shown in Table (4.1).

This could be explained by interionic attraction, i.e. with increase in salt concentration the activity of Ca ions decreased. This would lead to an increase in the mobilization of Ca ions from $CaCO_3$ in the solution, or could be related to the formation of ion pairs when Mg salt was added.

The variation in the mobilization of Ca ionsfrom $CaCO_3$ between two different salts added can be explained as follows :-

In the case of NaCl salt for example, every calcium ion is surrounded by chloride ions and every carbonate ion is surrounded by sodium ions thereby decreasing the activity of both of them. To give the same dissociation constant, the concentration of Ca and CO_3 ions in solution must increase.

It was found that in most cases $MgCl_2$ increased the solubility of Ca more than NaCl. This is due to the higher ionic strength of $MgCl_2$ than NaCl (valency effect) as mentioned previously in the introduction to this chapter. The increase in the ionic strength has a tendency to increase the solubility of the compound (Garrles and Christ 1965).

A comparison of the results (in duplicate) for individual and mixed samples of salt, added at two concentrations (10 and 40 meq/l) showed a marked increase in the solubility of Ca in the case of the mixture (NaCl + $MgCl_2$). This increase was less with $MgCl_2$. With NaCl the increase in the solubility of Ca was found to be less than the two examples mentioned above ($MgCl_2$ and the mixture of salt) as shown in Table (4.1).

At 10 meq/l of salt added, it was found to be 0.5 meq/100 ml for NaCl, 0.8 meq Ca/100 ml for $MgCl_2$ and 0.9 meq Ca/100 ml for the mixture (NaCl + $MgCl_2$).

But at 40 meq/l the comparable figures were 0.6 meq Ca/100 ml for NaCl, 0.9 meq Ca/100 ml for $MgCl_2$ and 1.2 meq Ca/100 ml for mixture (NaCl + $MgCl_2$).

In the case of the mixture of NaCl + $MgCl_2$, the increase in the solubility of Ca may be related to the increase in the ionic atmosphere of ions in the solution which leads to a decrease in the activity of Ca ions thus resulting in an increase in the concentration of Ca ions in the solution. In addition the ion pair effect may increase the mobilization of Ca ions from $CaCO_3$. The relatively greater stability of $MgCO_3$ ion pairs would suggest that Mg exerts an important indirect control on $CaCO_3$ solubility which results in a redistribition of CO_2 from the atmosphere which effects the pH of the solution, and hence increases the solubility of Ca.

In order to see whether the valency or the concentration of salts effect the dissociation of Ca from $CaCO_3$, two experiments were carried out :-

(1) The effect of SO_4 and Cl salts of Na, K and Mg on the solubility of $CaCO_3$ was tested by shaking these salts with

soil treated with 1.0 gm of $CaCO_3$ as mentioned later in Section (4.3.2).

(2) The effect of NaCl, $MgCl_2$ and NaCl + $MgCl_2$ on the solubility of $CaCO_3$ was tested by leaching with these salts soil treated with 1 gm $CaCO_3$. This experiment was selected because it could be carried out in a short period of time and is more or less similar to the natural conditions found in the soil. The results are shown in Table (4.2). From this Table it was found that the results from the leaching experiment were not as predicted. The change in the order of the effect of salts on the solubility of Ca between the shaking experiment and the leaching experiment could firstly be related to the effect of salts on the physical properties of soil and also due to the time of contact of each of the salts with the soil.

To control the above mentioned interferences, this experiment was repeated in duplicate by shaking as in Section (4.3.3).

4.3.2 The effect of sulphate and chloride salts of Na, K and Mg on the solubility of $CaCO_3$ by shaking with soil treated with 1 gm $CaCO_3$:

The effect of salts on the mobility of Ca ions from the soil treated with 1 gm $CaCO_3$/10 gm soil was found to be more in the case of SO_4 than Cl , as shown in Table (4.4). This may be related to the formation of ion pairs with SO_4 but not with Cl .

In sub soil it was found that the effect of salts on the mobilization of Ca ions are in the following order :-

$$K = Mg > Na \quad \text{for } SO_4$$

$$K > Mg > Na \quad \text{for } Cl$$

But in top soil at 40 meq/l the order was :-

$Mg > K > Na$ as shown in Table (4.4)

This may be related to the difference in the dissociation constants of Mg, K and Na ion, as shown in Table (4.3). This reflects the degree and nature of the complex of various ionic pairs, which decreases the activity of Ca ions.

The difference between K and Na salts may be related to differences in the mobility or the activity of these ions. There is a function of size and degree of hydration as follows :- (Jenney and Retemerier 1935)

ions	dehydration radii	hydration radii
Na	0.98 Å	7.90 Å
K	1.33 Å	5.32 Å

The change in the order noted from SO_4 to Cl salt may be attributed to the complex formation with Mg which does not form with K salt. The overall effect is to reduce the effect of Mg salts to a degree which is either equivalent to K_2SO_4 or less than KCl in the case of Cl salts or may be related to the actual concentrations of these salts in soil.

It was found that SO_4 increases the mobilization of Ca from $CaCO_3$ more than Cl. This could be due to the valency effect, which exerts more effect in decreasing the activity of Ca than Cl salt. This leads to an increase in the mobilization of Ca from $CaCO_3$ in the solution.

4.3.3 The effect of salts (NaCl, $MgCl_2$ and NaCl + $MgCl_2$) on the solubility of $CaCO_3$ by shaking with soil treated with 1 gm $CaCO_3$:

The effect of salts on the solubility of $CaCO_3$ by shaking with soil treated with 1 gm of $CaCO_3$ was carried out to control the errors of the leaching experiment. The results are shown in Table (4.3).

The solubility of Ca is greatly increased in the presence of salts viz:- 1.6 meq Ca/100 gm in the case of distilled water, 15.0 meq Ca/100 gm for NaCl, 15.4 meq Ca/100 gm for $MgCl_2$ and 25.6 meq Ca/100 gm for the mixture (NaCl + $MgCl_2$).

This effect with $MgCl_2$ was found to be slightly more than with NaCl but it was much higher when they were mixed. It was more than one and a half times greater in the case of the mixture.

This increase in the solubility of calcium could be related to the increase in the ionic atmosphere of ions in the solution which would lead to a decrease in the activity of Ca ions, thereby increasing the concentration of Ca ions in the solution.

Table (4.1)

The effect on the mobility of $CaCO_3$ when shaking with salt solution ($CaCO_3$ suspension + salt)

Conc. meq/l salt added	In presence of $CaCO_3$ 0.1 gm			In presence of 1.0 gm $CaCO_3$	
	meq Ca / 100 ml				
	NaCl	$MgCl_2$	NaCl + $MgCl_2$	NaCl	$MgCl_2$
0	0.3	0.3	nd	0.5	0.5
2	0.3	0.4	nd	0.5	0.5
5	0.5	0.6	nd	0.6	0.6
10	0.5	0.8	0.9	0.8	0.9
40	0.6	0.9	1.2	0.8	1.0
60	0.6	0.9	nd	0.9	1.1
80	0.6	1.0	nd	0.8	1.1
100	0.6	1.2	nd	0.9	1.3

nd = not determined

The results are the mean of duplicates

Table (4.2)

The effect on the mobility of $CaCO_3$ when (soil + $CaCO_3$) was leached with salt solution

Aliquot	meq Ca / 100 gm oven dry soil			
	NaCl 1000 meq/l	$MgCl_2$ 1000 meq/l	NaCl + $MgCl_2$ 500 meq/l 500 meq/l	H_2O
1st	25.6	15.4	26.6	15.4
2nd	3.7	2.5	3.3	2.4
3rd	2.1	1.4	1.7	1.3
4th	1.6	1.2	1.3	0.3

Table (4.3)

The effect on the mobility of $CaCO_3$ when (soil + $CaCO_3$) was shaken overnight (17 hours) in 1:10 soil solution ratio

meq Ca /100 gm oven dry soil			
NaCl 1000 meq/l	$MgCl_2$ 1000 meq/l	NaCl + $MgCl_2$ 500 meq/l 500 meq/l	H_2O
25.6	15.4	25.6	1.6

The results are the mean of duplicates.

Table (4.4)

The effect of salts of Na, K, Mg on the solubility of $CaCO_3$ by shaking with 1 gm $CaCO_3$

A - Brown earth top soil meq Ca/100 gm oven dry

Conc. meq/l	NaCl	Na_2SO_4	KCl	K_2SO_4	$MgCl_2$	$MgSO_4$
10	1.2	1.5	1.3	2.0	1.7	2.2
40	2.2	2.7	3.0	3.9	3.6	4.0

B - Brown earth sub soil meq Ca/100 gm oven dry

Conc. meq/l	NaCl	Na_2SO_4	KCl	K_2SO_4	$MgCl_2$	$MgSO_4$
10	1.8	2.2	2.7	2.4	2.4	2.4
40	3.1	3.2	4.6	4.7	3.9	4.7

The results are the mean of duplicates

Table(4.5)

Dissociation constants for some dissolved species in aqueous solution at 25°C (Garrels and Christ (1965)

Cations	OH	HCO_3	CO_3	SO_4	Cl
K	-	-	-	0.96	-
Na	- 0.7	- 0.25	1.27	0.72	-
Ca	1.30	1.26	3.20	2.31	-
Mg	2.18	1.16	3.4	2.36	-
H	14.0	6.4	10.33	2.0	-

Table (4.6)

Distribution of major dissolved species in sea water (9% chlorinity, 25°C, pH 8.15) (Garrels and Christ 1965)

ion	Molality (Total)	Free ion %	Me – SO_4 pair %	Me – HCO_3 pair %	Me – CO_3 pair %
Na	0.48	99	1	–	–
K	0.010	99	1	–	–
Mg	0.054	87	11	1	0.3
Ca	0.010	91	8	1	0.2

ion	Molality	Free ion %	Ca – Anion pair %	Mg – Anion pair %	Na – Anion pair %	K – Anion pair %
SO_4	0.028	54	3	22	21	0.5
HCO_3	0.0024	69	4	19	8	–
CO_3	0.00027	9	7	67	17	–
Cl	0.56	100	–	–	–	–

Table (4.7)

Activity coefficients of individual species in sea water (ionic strength 0.7 chlorinity 19‰, 25°C) (Garrels and Christ 1965)

Dissolved species	Activity coefficient	Method used
$NaHCO_3^{\circ}$	1.13	Analogy with H_2CO_3
$MgCO_3^{\circ}$	1.13	" " "
$CaCO_3^{\circ}$	1.13	" " "
$MgSO_4^{\circ}$	1.13	" " "
$CaSO_4^{\circ}$	1.13	" " "
HCO_3^-	0.68	From activity coefficient of $KHCO_3$, K_2CO_3
$NaCO_3^-$	0.68	Analogy with HCO_3^-
$NaSO_4^-$	0.68	" " "
KSO_4^-	0.68	" " "
$MgHCO_3^+$	0.68	" " "
$CaHCO_3^+$	0.68	" " "
Na^+	0.76	Meas. glass electrode
K^+	0.64	$YK^+ = Y \pm KCl$
Mg^{2+}	0.36	$Y\ Mg^{++} = Y^3 \pm MgCl_2 (Y^3 \pm KCl)$
Ca^{2+}	0.28	$Y\ Ca^{++} = (Y^3 \pm CaCl_2)\ (Y^2 \pm KCl)$
Cl^-	0.64	$Y\ Cl^- = Y \pm KCl$
$CO_3^=$	0.20	$Y\ CO_3^=$ based on K_2CO_3 solution
$SO_4^=$	0.12	$Y\ SO_4^=$ as a function of the ionic strength

CHAPTER FIVE

THE EFFECT OF SALT ON THE SOLUBILITY OF NATIVE CATION FROM SOIL

5.1 INTRODUCTION

Changes in the relative and total concentrations of cations are simultaneously accompanied by shifts in the exchangeable base status of the soil, because of the equilibrium existing between soluble and exchangeable cations. The exchangeable and solution forms are in dynamic equilibrium.

The deficiency of ions in solution may be due to losses in drainage water, absorption by organisms, reprecipitation of a secondary compound or adsorption on to surrounding clay particles.

Weigner arranged the cations in the order of their replacing power, which is the Hofmeister lyotropic series as follows :-

$$Na < K \quad \text{and} \quad Mg < Ca$$

The replacing power depends on the kind of cation being replaced and the kind of exchange material, also the ion size and hydration. Wiegner and Jenny (1927) found that the replacing power increased, e.g. for Na ions, by adding alcohol to the solution. (An increase in hydration radius decreases the activity of ions).

This experiment was carried out to assess the influence of the cation exchange capacity and equilibrium constants of salts (due to lyotropic series), and to consider the findings in terms of the Donnan equilibrium equation for the distribution of ions in the ionic atmosphere (see Chapter Three, Section 3.1.4).

A series of analysis was carried out to test the effect of different salts on the solubility of cations (Na, K, Ca, Mg). This experiment should give an idea of the effect of individual salt on the solubility of cations and indirectly their availability to plants.

The salts used were NaCl, Na_2SO_4, KCl, K_2SO_4, $MgCl_2$, $MgSO_4$, $CaCl_2$, $CaSO_4$ and the native cations were Na , K , Ca and Mg .

These cations were selected because they are considered to be involved in saline soils, while Cl and SO_4 are the chief anions (Hesse 1971). In addition, the ions mentioned above affect indirectly the solubility of essential nutrients for plant growth (e.g. phosphate).

Potassium interferes competitively with the absorption of a number of ions (Wadleigh and Shive 1939).

Thomas and Mack (1939) found that high K absorption depressed the absorption of Ca and Mg . Stanford et al (1941) added K to a soil high in Ca and Mg carbonates and showed a reduced Ca and Mg uptake.

Collander (1941); Troug et al (1953) and Harmer et al (1953) have investigated the response of different crops to applied sodium. The response of crops to sodium in the presence or absence of K was stated by Harmer and Benne (1945) as shown in Table (5.1).

Mg is the component of chlorophyll and it is also connected with phosphorus metabolism (Zimmerman 1947).

For further information on nutrient deficiencies and symptoms in plants consult Agrios (1969).

5.2 METHODS

5.2.1 Effect of salt on ion solubility:

For these experiments only the top and sub soil samples of saline gleyed soil and non saline brown earth soil samples were used. The muck soil was not included as it had been polluted or contaminated by industrial sewage discharged into the river. For the following studies –

The salts NaCl, Na_2SO_4, $MgCl_2$, $MgSO_4$, KCl, K_2SO_4, $CaCl_2$, and $CaSO_4$ were added to the samples at a series of low and high concentrations, namely 0, 2, 5, 10 meq/l and 40, 60, 80 meq/l and a 1:10 soil/water ratio. X gm of salt was weighed accurately directly into a weighing bottle and transferred to 1000 ml volumetric flask, and the sample diluted to volume — Stock solution (A).

100 ml of stock solution (A) were added to 10 gm air dry soil (. brown earth soil sample and gleyed soil sample both top and sub soil). They were shaken on a rotary shaker for 16 hours at 18 – 21°C. The soil suspension was filtered through Whatman No 42 filter paper to give a clear extract and soluble cations measured.

Na and K were measured by flame emission (EEL) Mg and Ca ions were measured by atomic absorption after the extract had been treated with 5% La as $La(NO3)_3$ $6H_2O$ salt to prevent interference by phosphate.

NOTE: X gm of salts were weighed as powders equivalent to 0, 2, 5, 10, 40, 50, 60, 80 meq/l of NaCl, Na_2SO_4, KCl, K_2SO_4, MgCl, $MgCl_2$, $MgSO_4$, $CaCl_2$ and $CaSO_4$.

5.3 Results and Discussion:

As mentioned in the introduction to this chapter the predicted order of displacement of cations is Ca > Mg > K > Na, while with anions it is $SO_4 > Cl$. This is due to the hydration and valency effects as discussed previosuly in Chapter Four.

At higher concentrations, many more factors are involved. These factors include :-

(1) Precipitation of $CaSO_4$ (solubility of salts)

(2) Formation of ion pairs which decreases the activity of ions

(3) Actual amount of cations in soil

(4) The relative concentration of such cations in the exchangeable bases.

It was found in practice that with the brown earth top soil, the displacement of cations both in dilute and high concentration of applied salt was, as expected, the order being :-

Ca > Mg > K > Na as shown in Table (5.2)

With regard to the anions the order of displacement of cations from dilute solution was as expected ($SO_4 > Cl$), while in high concentration the order of displacement of divalent cations (Mg or Ca) was greater in the case of added Cl than SO_4 as shown in Table (5.2).

This could be related to the formation of ion pairs with SO_4 in high concentration which obviously decreases the the activity of the salt and then reduces its displacing power. Cl ions on the other hand do not form ion pairs with any cation (Garrels and Christ 1965) and were therefore less affected by concentration effects.

In brown earth sub soil it was found that the displacement of cations in dilute and concentrated solutions of applied salt is in the order of the valency and the lyotropic series, except for dilute solutions of Na_2SO_4 when the order was ($Ca > K > Mg$). On the other hand in high concentration the exception was with the additions of K_2SO_4 and $CaCl_2$. It was found that for K_2SO_4 Na ions were displaced more than Mg ions, while with $CaCl_2$ the displacement of Na ions was more than K ions as shown in Table (5.3).

It was found that in brown earth sub soil, SO_4 displaces more cations than Cl except for monovalent salts when the displacement of Mg was greater for Cl than SO_4.

With Mg salts the displacement of Na and K was greater for Cl than for SO_4. However, in the case of Ca salts there is no anomalies in dilute solution as shown in Table (5.3).

At high concentration however Cl displaces more than SO_4 except in the case of the Na salt. The displacement of the divalent cations (Ca, Mg) was in the order $SO_4 > Cl$. The other exception was with K and Mg salts where the displacement of Na was in the order $SO_4 > Cl$. This also applied to Ca when K salt was added as shown in Table (5.3).

The complete set of results of the effect of salt on the displacement of cations in gleyed soil are presented in Table (5.4).

It will be noted that several exceptions to the predicted order were recorded as noted above with brown earth soil, e.g. it was found that the displacement of cations at high and low concentration of salt added in the case of Cl was more than for SO_4, while in the case of added sodium salt the order was $Ca > Mg > K$ for Cl and $Mg > K > Ca$ for SO_4, as shown in Tables (5.4) and (5.5).

It was found that the SO_4 salt of Na displaced K ions more than Cl salt in top soil, but with other ions and with sub soil the behaviour was not anomalous. The other exception was the Ca ion which was found to be increased by the addition of NaCl, but decreased by the addition of Na_2SO_4 in both top and sub soil, as shown in Tables (5.4) and (5.5).

The addition of Ca salts gave the opposite effect to the Mg salt in the top soil Cl salt displacing ions more than SO_4, while in the sub soil the SO_4 displaced twice as much of the ions as the Cl salt.

From these preliminary analysis the following tentative conclusions can be drawn :-

(1) Uni-univalent salt (NaCl, KCl):
In brown earth for top and sub soils, KCl displaced Ca and Mg ions more than NaCl as presented in graphical form (1,3) and (9,11).

In gleyed soil, it was found that for both top and sub soil, NaCl displaced Ca more than KCl as presented in graphical form (5,7), while KCl displaced Mg more than NaCl as presented in graphical form (13,15).

(2) Bi-univalent salt (K_2SO_4, Na_2SO_4):
The ability of K_2SO_4 to displace Ca and Mg ions was greater than for Na_2SO_4 for both top and sub soil in both soils (gleyed and brown earth) as presented in graphical form (2,4) and (10,12) for brown earth soil, and (6,8) and (14,16) for gleyed soil.

(3) Unibivalent salt ($CaCl_2$, $MgCl_2$):
For both brown and gleyed soil the ability of $CaCl_2$ to displace K was more than $MgCl_2$ as presented in graphical form (17,21), while in sub soil for both soils no anomalies were found.

In gleyed top soil the ability of $MgCl_2$ to displace Na was more than $CaCl_2$, but the opposite was true with sub soil ($CaCl_2$ displaced Na more than $MgCl_2$) as presented in graphical form (29,31).

With the brown earth soil no order could be recognised for the displacement of Na ions.

(4) Bibivalent salt ($MgSO_4$, $CaSO_4$):

The ability of $MgSO_4$ to displace K ions was greater than for $CaSO_4$ in both top soil samples (gleyed and brown earth) as presented in graphical form (18,22).

The opposite was true in sub soil, i.e. $CaSO_4$ displaced K ions more than $MgSO_4$, as presented in graphical form (20,24).

In gleyed soil the ability of $MgSO_4$ to displace Na ions was more than $CaSO_4$, as presented in graphical form (30).

As noted above when the many results obtained above are considered in terms of their predicted order of displacement based on CEC, hydration etc., several exceptions were found, some of which can be explained in terms of ion pairs, insolubility and actual amounts of ions in soil. Less problems are experienced in dilute solutions as expected. However, these results were of a somewhat tentative nature but do highlight one or two areas of interest in need of further study, viz: the efficiency of Na ions etc., in replacing cations in the sub soil samples. This could not be accounted for solely in terms of entrained salt. Also of note is the selectivity exhibited by plants in the uptake of K/Na compared with what is in the solution of the soil, see Table (2.6) and Table (2.8). Ratios of K/Na in solution from gleyed top and sub soil of 0.34, 0.38 respectively and from plants grown on gleyed soil of K / Na 0.03 were obtained.

Table (5.1)

The response of crops to sodium in the presence or absence of K (Harmer and Benne 1945)

Degree of benefit with a deficiency of potassium		Degree of benefit with sufficient potassium	
None to slight	Slight to medium	Slight to medium	Large
Buchwheat	Barley	Cabbage	Celery
Lettuce	Broccoli	Kale	Mangols
Maize	Brussels sprouts	Kohlrabi	Sugar-beet
Potato	Carrot	Mustard	Swiss chard
Rye	Cotton	Radish	Table beet
Soybean	Millet	Rape	Turnip
Spinach	Oat		
Strawberry	Pea		
Sunflowers	Tomato		
White bean	Wheat		

Table(5.2)

Comparison of the solubility of different cations in the presence of the same salt for brown earth top soil meq cation/100 gm soil

	NaCl			Na_2SO_4			KCl			K_2SO_4			$MgCl_2$			$MgSO_4$			$CaCl_2$			$CaSO_4$		
meq/l salt added	K	Ca	Mg	K	Ca	Mg	Na	Ca	Mg	Na	Ca	Mg	Na	K	Ca	Na	K	Ca	Na	K	Mg	Na	K	Mg
0	0.26	1.28	0.37	0.26	1.28	0.37	0.22	1.28	0.37	0.22	1.28	0.37	0.22	0.26	1.28	0.22	0.26	1.28	0.22	0.26	1.37	0.22	0.26	0.37
2	0.27	1.53	0.46	0.30	1.28	0.37	0.20	2.88	0.47	0.22	2.81	0.47	0.26	0.26	1.92	0.26	0.30	1.60	0.15	0.23	0.58	0.16	0.21	0.53
5	0.30	1.75	0.48	0.31	2.24	0.48	0.18	3.52	0.63	0.26	3.96	0.57	0.21	0.34	3.28	0.21	0.34	2.88	0.15	0.25	0.77	0.10	0.26	0.79
10	0.31	2.05	0.54	0.33	2.36	0.58	0.26	4.47	0.73	0.32	5.63	0.74	0.21	0.35	4.77	0.21	0.36	4.79	0.15	0.26	1.06	0.10	0.28	1.16
40	0.42	4.48	0.96	0.38	5.43	0.79	0.31	7.67	1.31	0.33	6.65	0.76	0.23	0.43	8.95	0.23	0.41	8.63	0.21	0.34	1.73	nd	nd	nd
60	0.42	4.60	1.04	0.43	6.23	0.9	0.34	8.63	1.36	0.44	8.31	0.80	0.21	0.47	11.83	0.21	0.44	9.59	0.22	0.74	6.23	nd	nd	nd
80	0.45	6.01	1.15	0.46	8.31	1.06	0.36	9.91	1.52	0.86	9.21	1.08	0.41	0.48	15.34	0.41	0.47	11.19	0.22	0.80	6.33	nd	nd	nd
10–0	0.05	0.77	0.14	0.07	1.08	0.21	0.04	3.19	0.36	0.10	4.35	0.37	–0.01	0.09	3.49	–0.01	0.10	3.51	0.07	0.34	0.69	–0.12	0.02	0.79
80–0	0.19	4.73	0.78	0.20	7.03	0.69	0.14	8.63	1.15	0.64	7.93	0.71	0.19	0.22	14.06	0.19	0.21	9.91	0.00	0.54	5.96	nd	nd	nd

Table (5.3)

Comparison of the solubility of different cations in the presence of the same salt for brown earth sub soil meq cation/100 gm soil

	NaCl			Na_2SO_4			KCl			K_2SO_4			$MgCl_2$			$MgSO_4$			$CaCl_2$			$CaSO_4$		
meq/l salt added	K	Ca	Mg	K	Ca	Mg	Na	Ca	Mg	Na	Ca	Mg	Na	K	Ca	Na	K	Ca	Na	K	Mg	Na	K	Mg
0	0.25	1.54	0.37	0.25	1.54	0.37	0.36	1.54	0.37	0.36	1.54	0.37	0.36	0.25	1.54	0.36	0.25	1.54	0.36	0.25	0.37	0.36	0.25	0.37
2	0.28	1.73	0.39	0.30	3.60	0.37	0.32	3.14	0.50	0.42	3.08	0.39	0.36	0.30	2.82	0.45	0.29	2.50	0.33	0.29	0.50	0.36	0.28	0.50
5	0.32	2.05	0.46	0.33	3.92	0.40	0.35	3.78	0.74	0.43	4.75	0.45	0.35	0.36	3.46	0.29	0.33	3.78	0.33	0.32	0.58	0.36	0.35	0.74
10	0.34	2.16	0.50	0.35	4.56	0.42	0.38	4.75	0.78	0.51	6.40	0.56	0.39	0.42	5.39	0.23	0.36	6.03	0.35	0.39	1.06	0.23	0.38	1.06
40	0.42	4.62	0.81	0.38	8.09	0.71	0.45	7.96	1.11	0.57	8.60	0.64	0.41	0.50	12.13	0.39	0.50	11.17	0.49	0.47	1.61	nd	nd	nd
60	0.46	5.14	0.86	0.43	0.70	0.85	0.50	9.24	1.24	1.05	10.40	0.73	0.43	0.45	12.77	0.36	0.53	11.49	0.64	0.49	1.65	nd	nd	nd
80	0.47	6.16	0.94	0.46	11.30	0.95	0.50	10.20	1.28	1.05	11.56	0.75	0.44	0.48	14.69	0.45	0.55	13.46	0.64	0.50	1.69	nd	nd	nd
10–0	0.09	0.62	0.13	0.10	3.02	0.05	0.02	3.21	0.41	0.15	4.86	0.19	0.03	0.17	3.85	–0.15	0.11	4.49	–0.01	0.14	0.69	–0.13	0.13	0.69
80–0	0.22	4.62	0.57	0.21	9.76	0.58	0.14	8.66	0.91	0.69	10.02	0.38	0.08	0.23	13.15	0.09	0.30	11.92	0.28	0.25	1.32	nd	nd	nd

nd = not determined

Results are the mean of duplicates.

Table (5.4)

Comparison of solubility of different cations in the presence of the same salt for gleyed top soil

meq cation/100 gm

meq/1 salt added	NaCl			Na$_2$SO$_4$			KCl			K$_2$SO$_4$			MgCl$_2$			MgSO$_4$			CaCl$_2$			CaSO$_4$		
	K	Ca	Mg	K	Ca	Mg	Na	Ca	Mg	Na	Ca	Mg	Na	K	Ca	Na	K	Ca	Na	K	Mg	Na	K	Mg
0	0.93	3.28	2.88	0.93	3.28	2.88	30.75	3.28	2.88	30.75	3.28	2.88	30.75	0.93	3.28	30.75	0.93	3.28	30.75	0.93	2.88	30.7	0.93	2.88
2	0.96	4.03	3.43	1.35	3.28	3.31	31.63	3.55	4.43	28.12	3.41	3.15	29.87	1.01	3.44	28.45	0.93	3.57	15.4	1.16	4.22	30.7	1.03	3.51
5	1.01	4.03	3.71	1.37	3.28	3.51	35.14	3.55	4.56	36.90	3.53	3.91	32.07	1.03	3.75	31.62	0.98	3.57	17.6	1.29	5.25	29.0	1.06	4.65
10	1.03	4.03	3.91	1.44	1.92	3.61	35.58	3.94	5.21	32.51	3.66	4.51	32.07	1.07	4.07	31.62	1.26	3.288	17.6	1.45	6,79	29.0	1.21	5.53
40	1.14	7.06	4.48	1.60	1.92	4.71	37.34	3.94	7.79	33.83	4.10	5.15	32.94	1.21	5.32	29.87	1.29	5.45	20.2	1.53	11.33	nd	nd	nd
60	1.16	8.44	5.77	1.64	1.92	4.91	43.05	4.34	8.42	37.78	4.42	5.35	32.07	1.23	5.64	31.19	1.34	6.08	21.5	1.89	12.46	nd	nd	nd
80	1.16	9.95	6.18	1.73	2.28	6.11	43.92	5.21	8.81	37.78	4.42	6.56	32.07	1.29	6.11	30.31	1.39	6.40	30.8	2.07	13.07	nd	nd	nd
10–0	0.1	0.75	1.03	0.51	–1.36	0.73	4.83	0.66	2.33	1.76	0.38	1.63	1.32	0.14	0.79	0.87	0.33	0.60	–13.15	0.52	3.91	– 1.7	0.28	2.65
80–0	0.23	6.67	3.3	0.8	–1.03	3.23	13.17	1.93	5.93	7.03	1.14	3.68	1.32	0.36	2.83	–0.44	0.46	3.12	0.05	1.14	10.19	nd	nd	nd

Table (5.5)

Comparison of solubility of different cations in the presence of some salt in gleyed sub soil

meq cation/100 gm soil

meq/1 salt added	NaCl			Na$_2$SO$_4$			KCl			K$_2$SO$_4$			MgCl$_2$			MgSO$_4$			CaCl$_2$			CaSO$_4$		
	K	Ca	Mg	K	Ca	Mg	Na	Ca	Mg	Na	Ca	Mg	Na	K	Ca	Na	K	Ca	Na	K	Mg	Na	K	Mg
0	0.96	3.32	2.92	0.96	3:32	2.92	33.83	3.32	2.92	33.85	3.32	2.92	33.83	0.96	3.32	33.83	0.96	3.32	33.83	0.96	2.92	33.83	0.96	2.92
2	0.89	4.09	2.92	0.99	3.32	3.08	37.41	3.85	6.19	31.17	3.32	3.18	33.85	1.09	3.32	35.63	1.0	3.64	36.85	0.96	3.05	41.87	1.20	3.40
5	1.04	4.09	3.28	1.0	1.6	3.18	39.20	4.12	6.71	34.74	3.68	3.70	34.30	1.12	3.64	39.19	1.26	4.28	36.85	1.06	3.13	32.07	1.33	4.40
10	1.11	4.47	3.48	1.01	1.28	3.39	34.30	4.44	6.78	37.41	3.96	4.17	36.52	1.16	3.96	37.86	1.26	4.59	37.29	1.17	3.73	37.41	1.46	5.45
40	1.21	7.67	5.48	1.11	1.6	4.77	36.97	4.52	7.14	38.30	4.22	4.80	36.97	1.25	4.44	36.52	1.28	5.23	37.74	1.38	12.53	nd	nd	nd
60	1.22	7.67	6.27	1.14	1.92	4.98	37.41	4.68	9.71	40.08	4.68	5.32	36.97	1.42	5.71	42.76	1.30	5.55	39.96	1.43	13.16	nd	nd	nd
80	1.23	8.82	6.74	1.18	2.56	5.93	38.31	5.32	10.62	40.08	5.09	6.36	37.86	1.48	6.67	40.97	1.36	5.87	41.30	1.48	13.57	nd	nd	nd
10–0	0.15	1.15	0.56	0.05	–2.04	0.47	0.45	1.12	3.86	3.56	0.64	1.25	2.67	0.20	0.64	4.01	0.30	1.27	3.44	0.21	0.81	3.56	0.5	2.53
80–0	0.27	5.50	3.82	0.22	–0.81	3.01	4.46	2.0	7.70	6.23	1.77	3.44	4.01	0.52	3.35	7.12	0.4	2.55	7.45	0.52	10.65	nd	nd	nd

nd = not determined.

Results are the mean of duplicate.

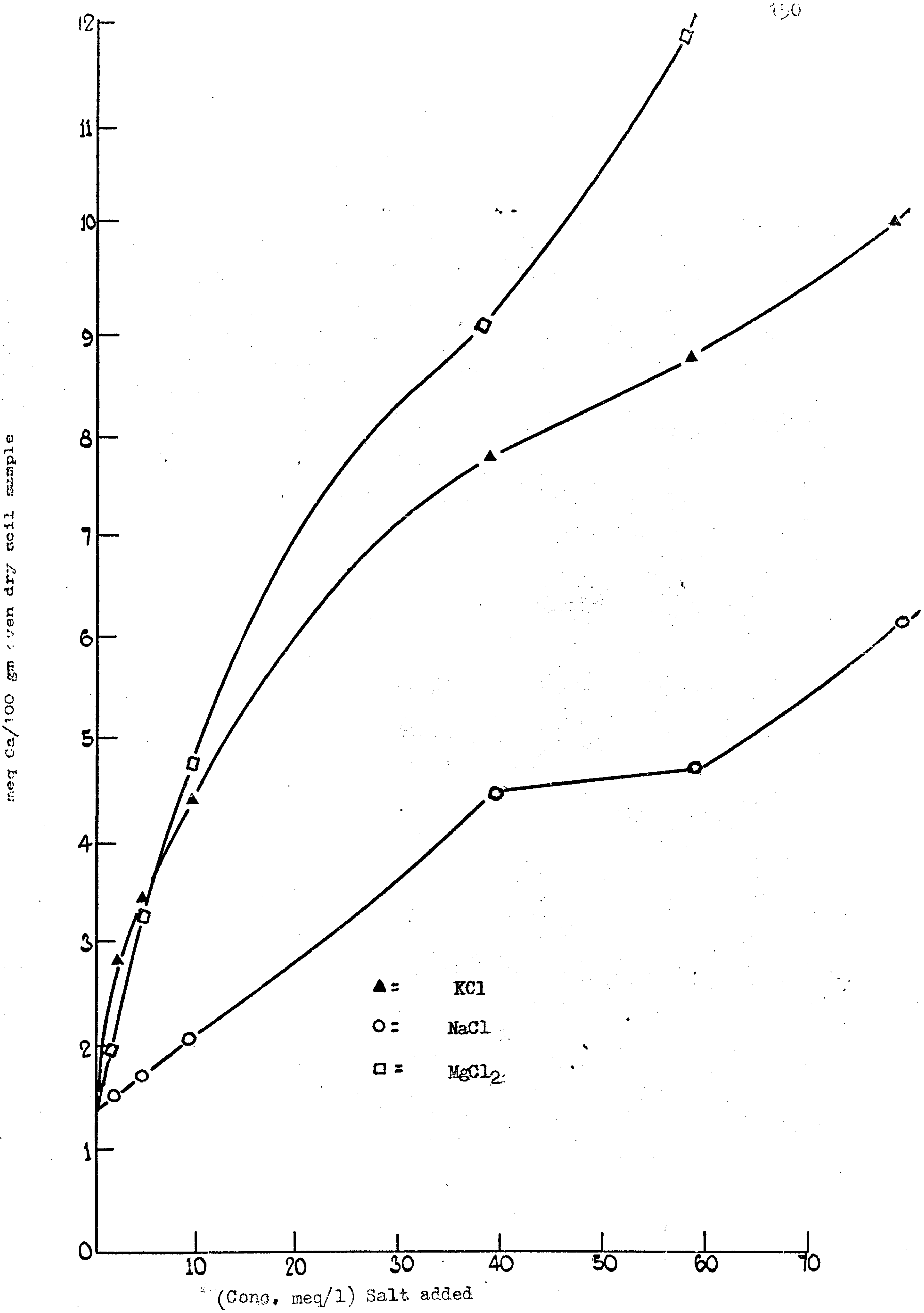


Fig. 1 The effect of salt on the displacement of native calcium from (BROWN EARTH TOP SOIL).

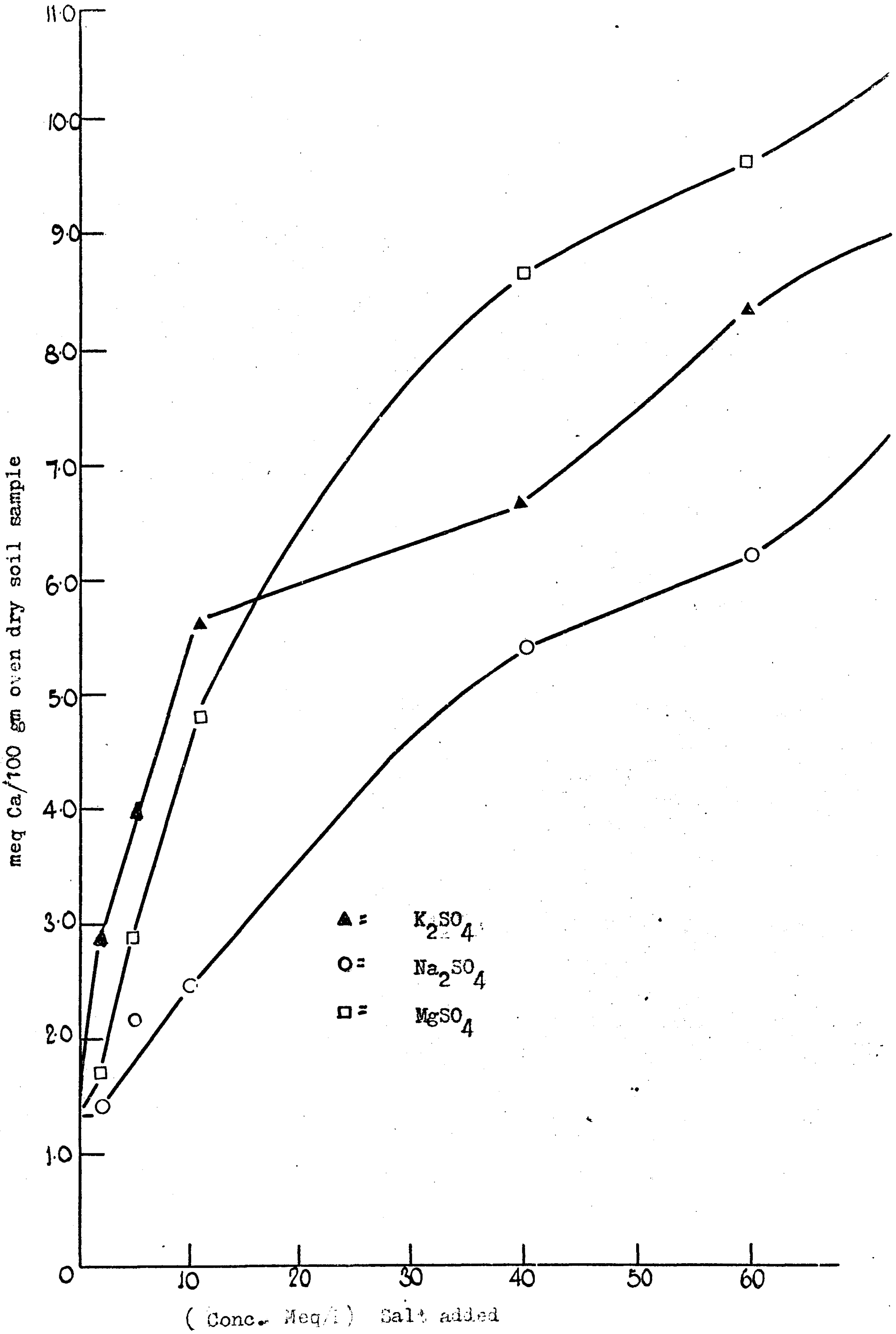


Fig. 2 The effect of salt on the displacement of native calcium from . (BROWN EARTH TOP SOIL).

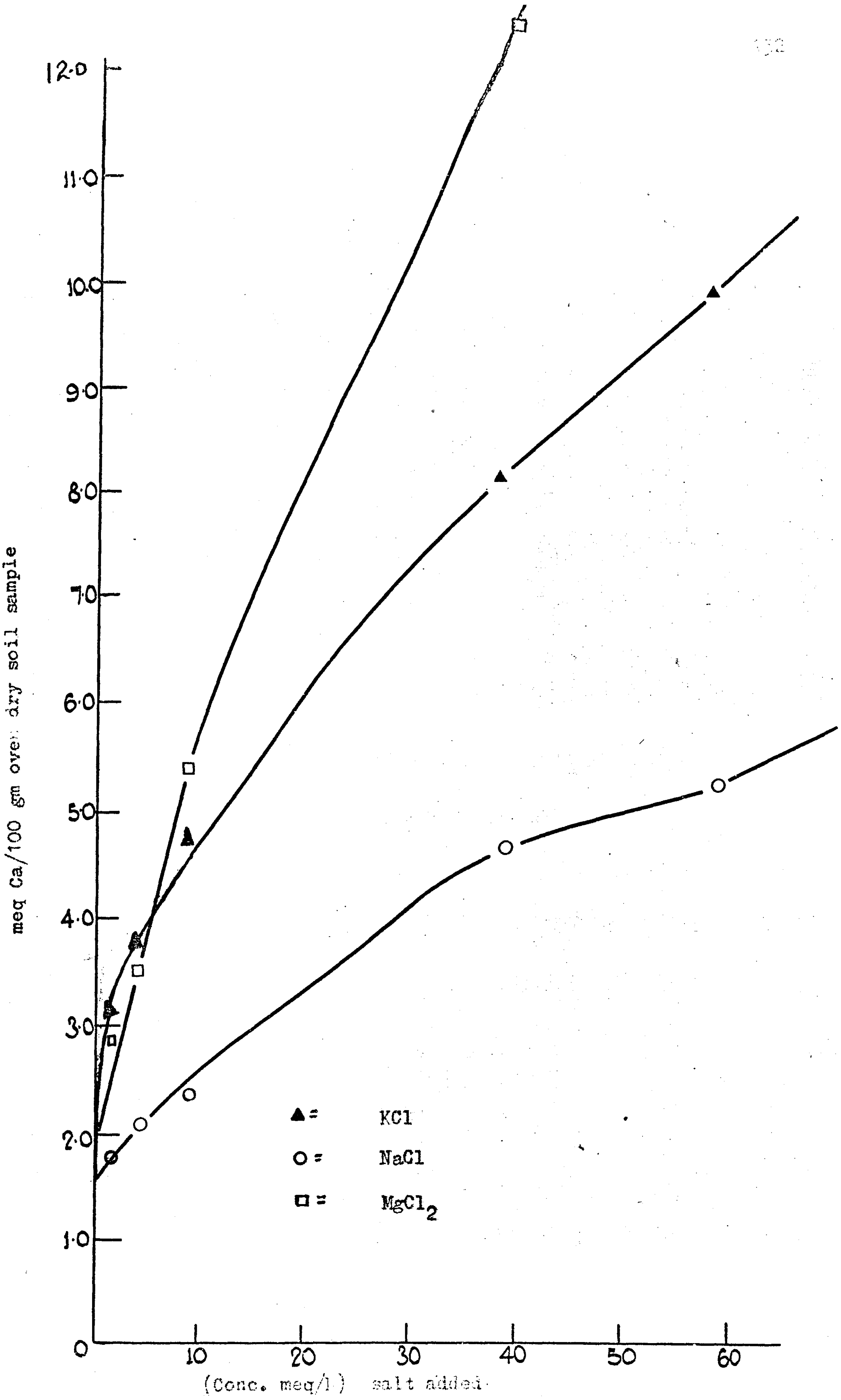


Fig. 3 The effect of salt on the displacement of native calcium fro

(BROWN EARTH SUB SOIL).

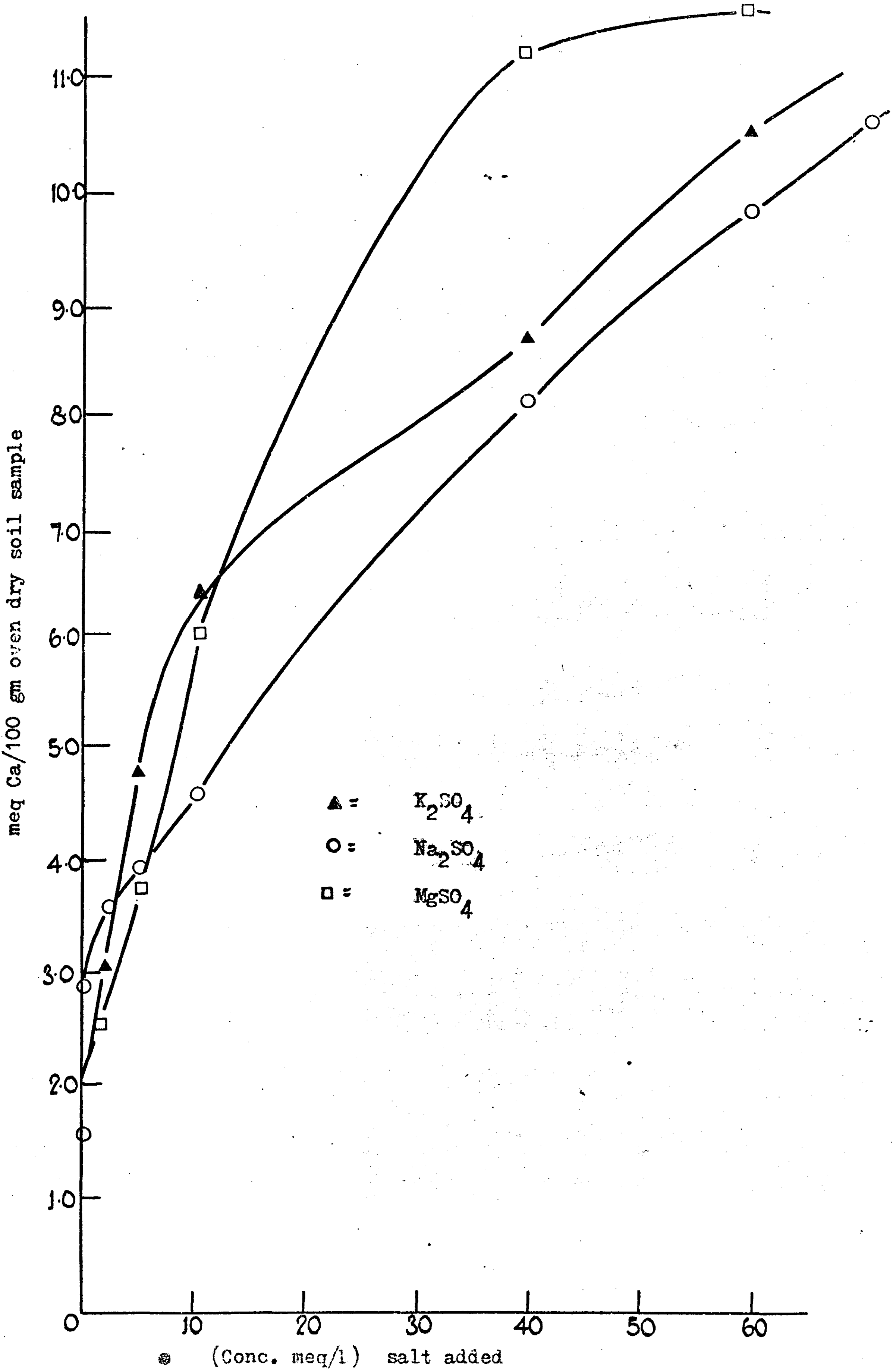


Fig. 4. The effect of salt on the displacement of calcium from (BROWN EARTH SUB SOIL).

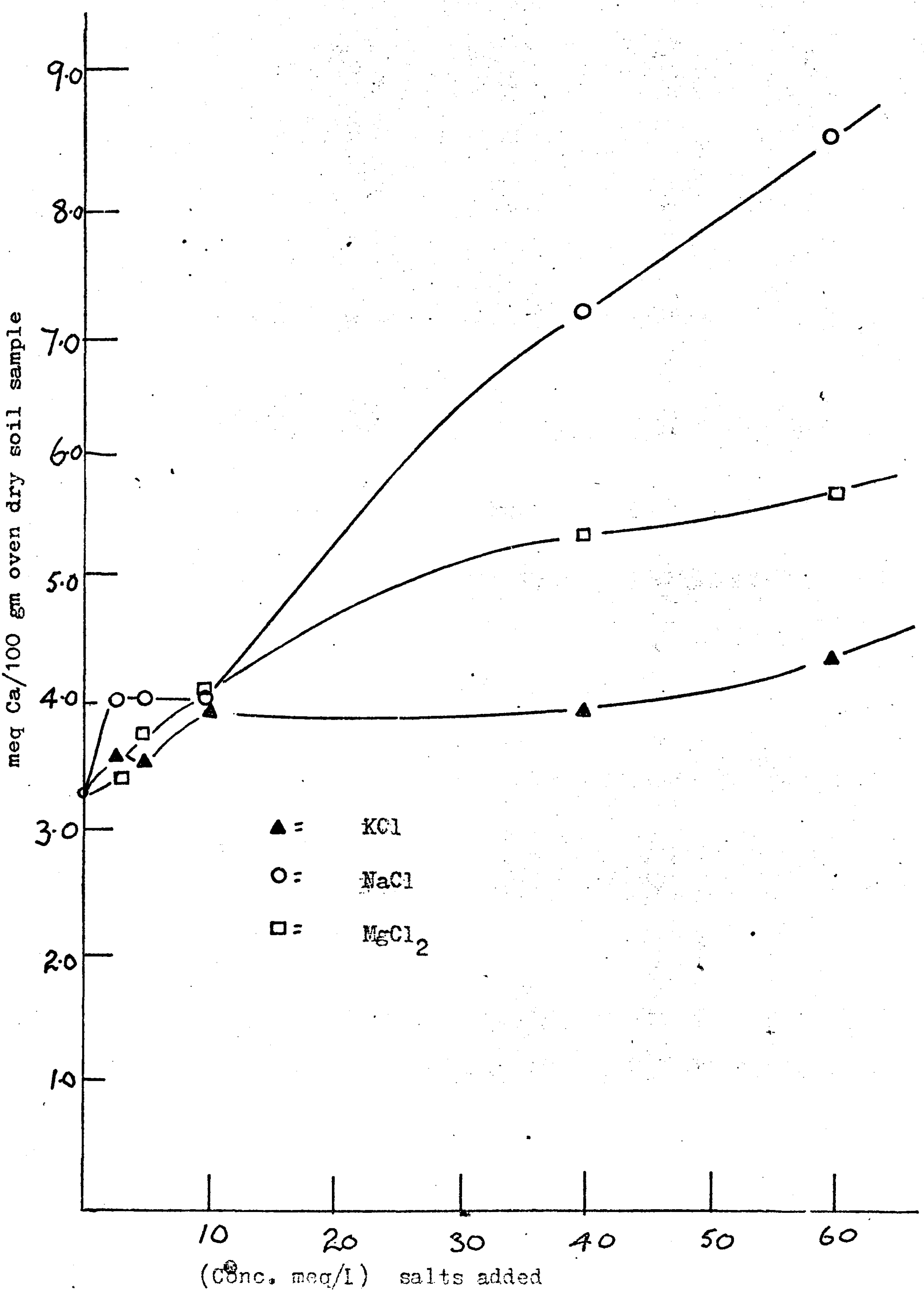


Fig. 5. The effect of salt on the displacement of native calcium from (GLEYED TOP SOIL).

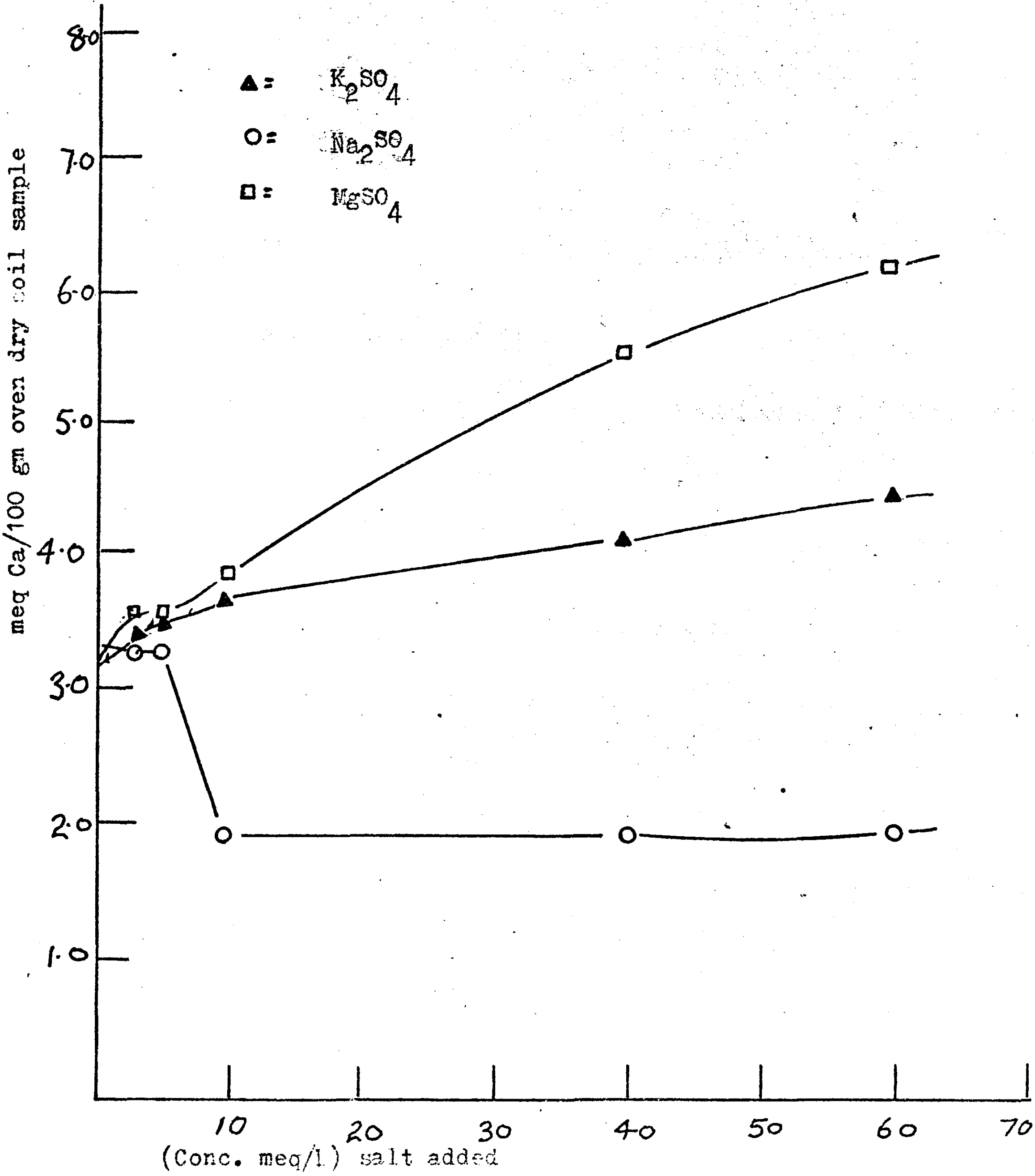


Fig. 6. The effect of salt on the displacement of native calcium from ([illegible]).

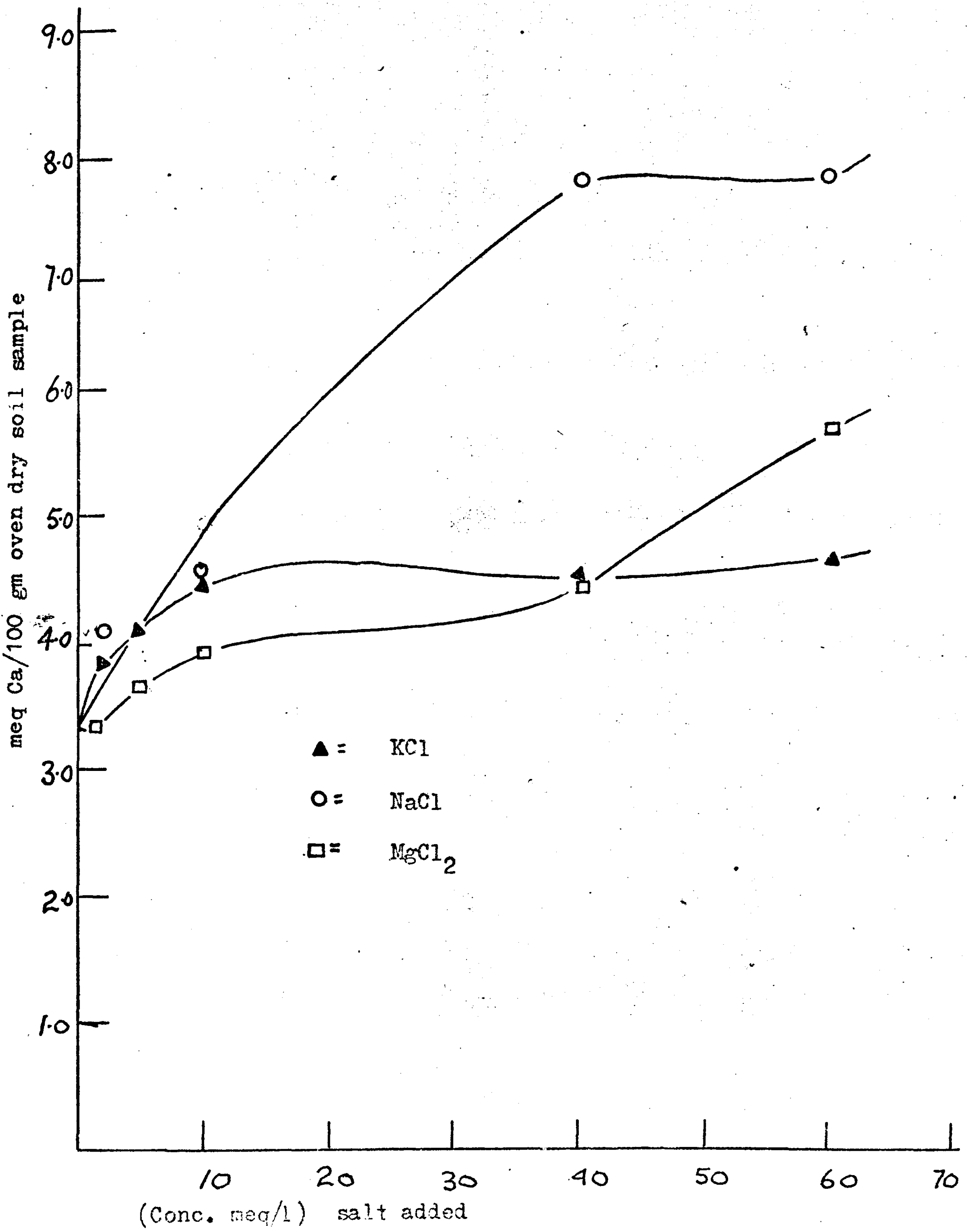


Fig. 7 Effect of salt on the displacement of native calcium from the ([illegible] SOIL).

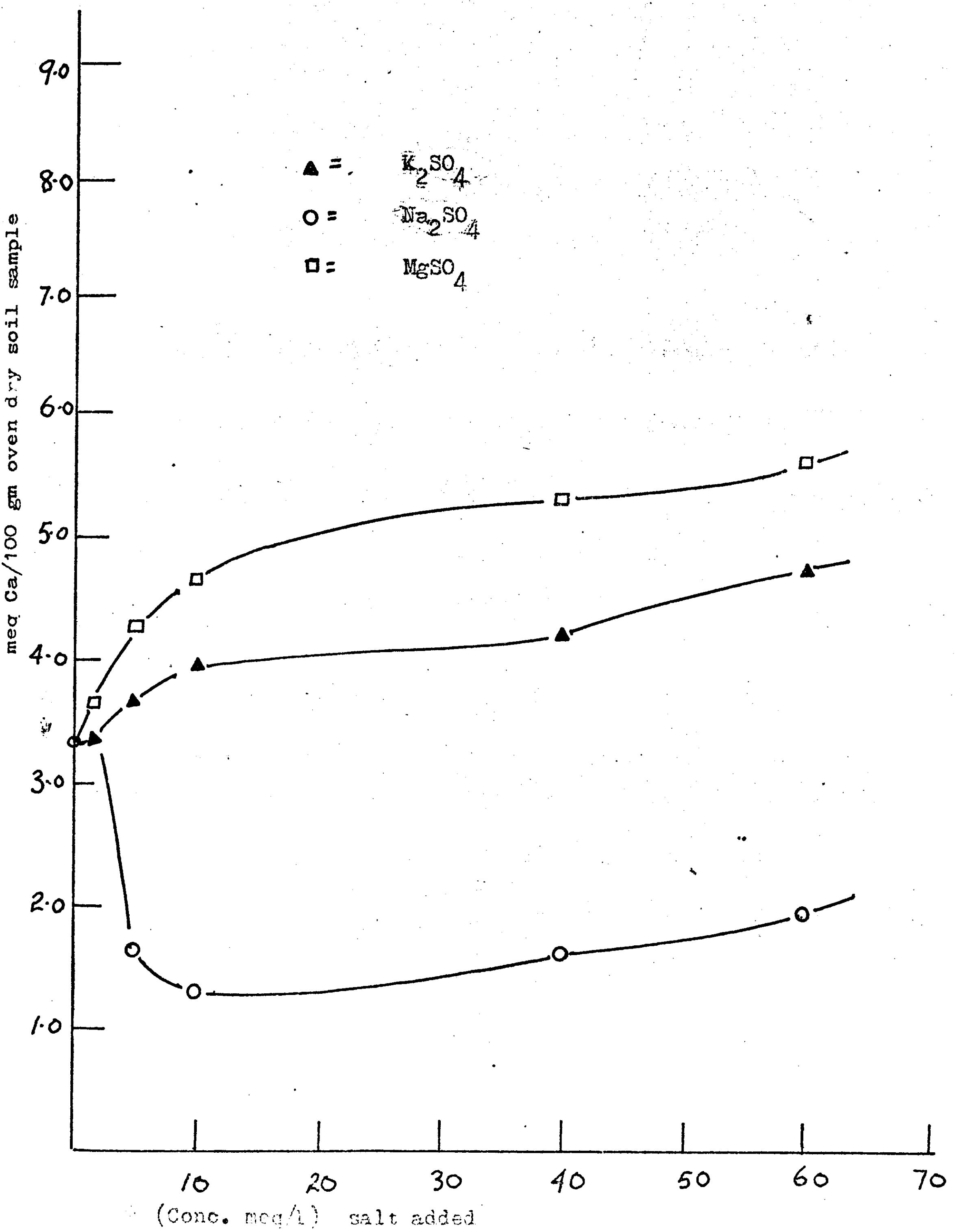


Fig. 6. The effect [illegible]
from , (CLEMSO SUB SOIL).

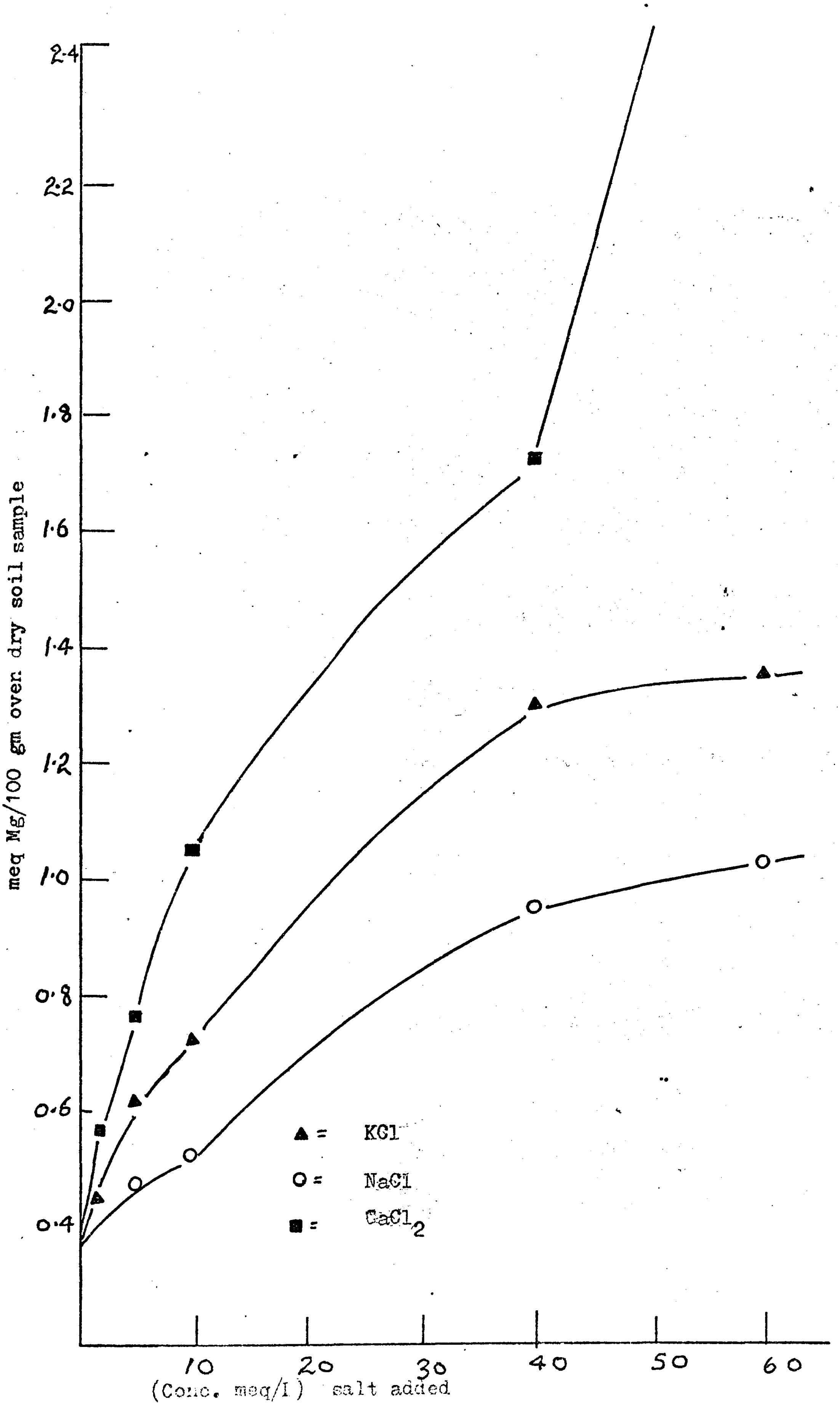


Fig. 9 The effect of salt on the displacement of native magnesium from ([illegible]).

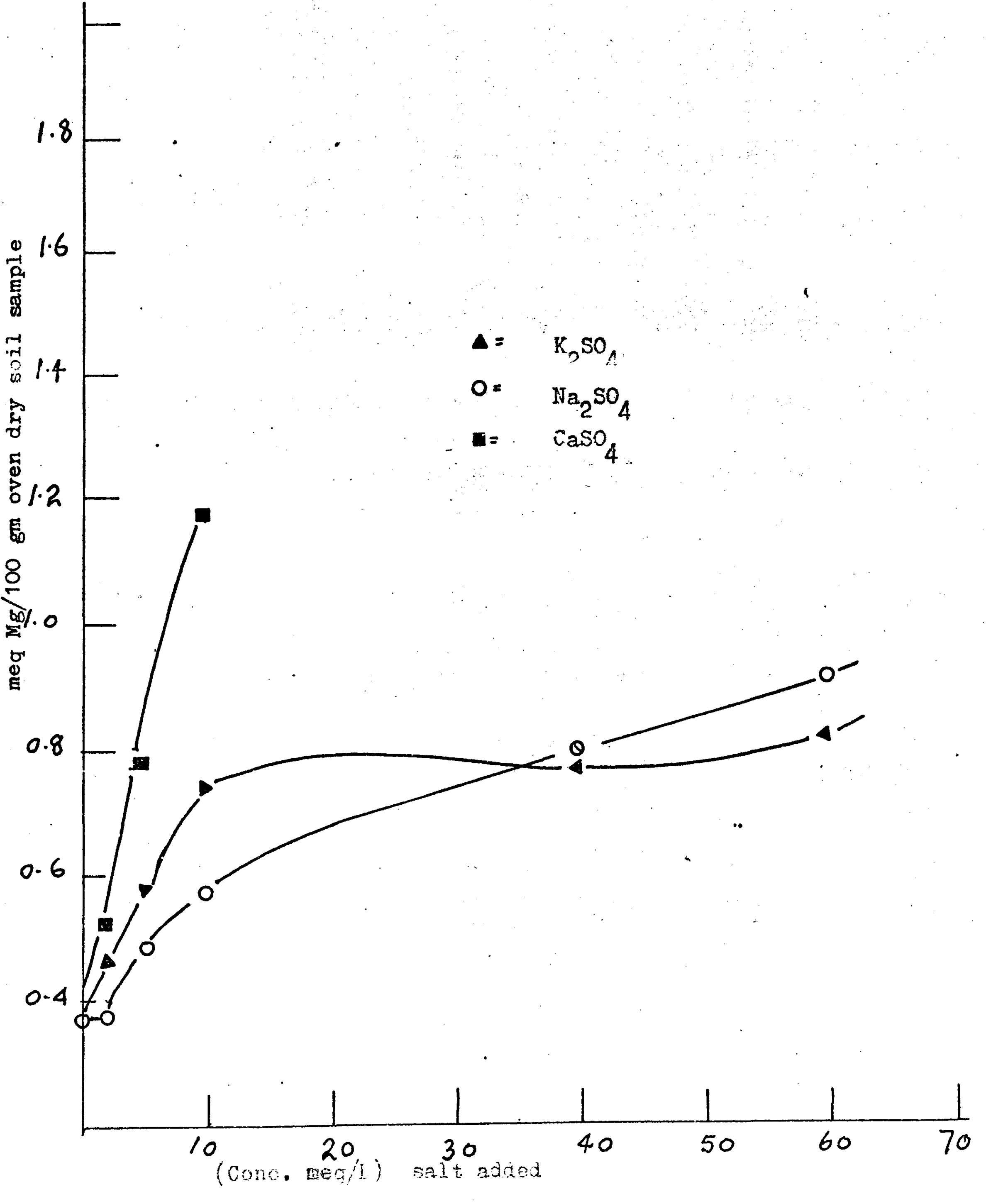


Fig. 10 Effect of salt on the displacement of native magnesium from the ([illegible]).

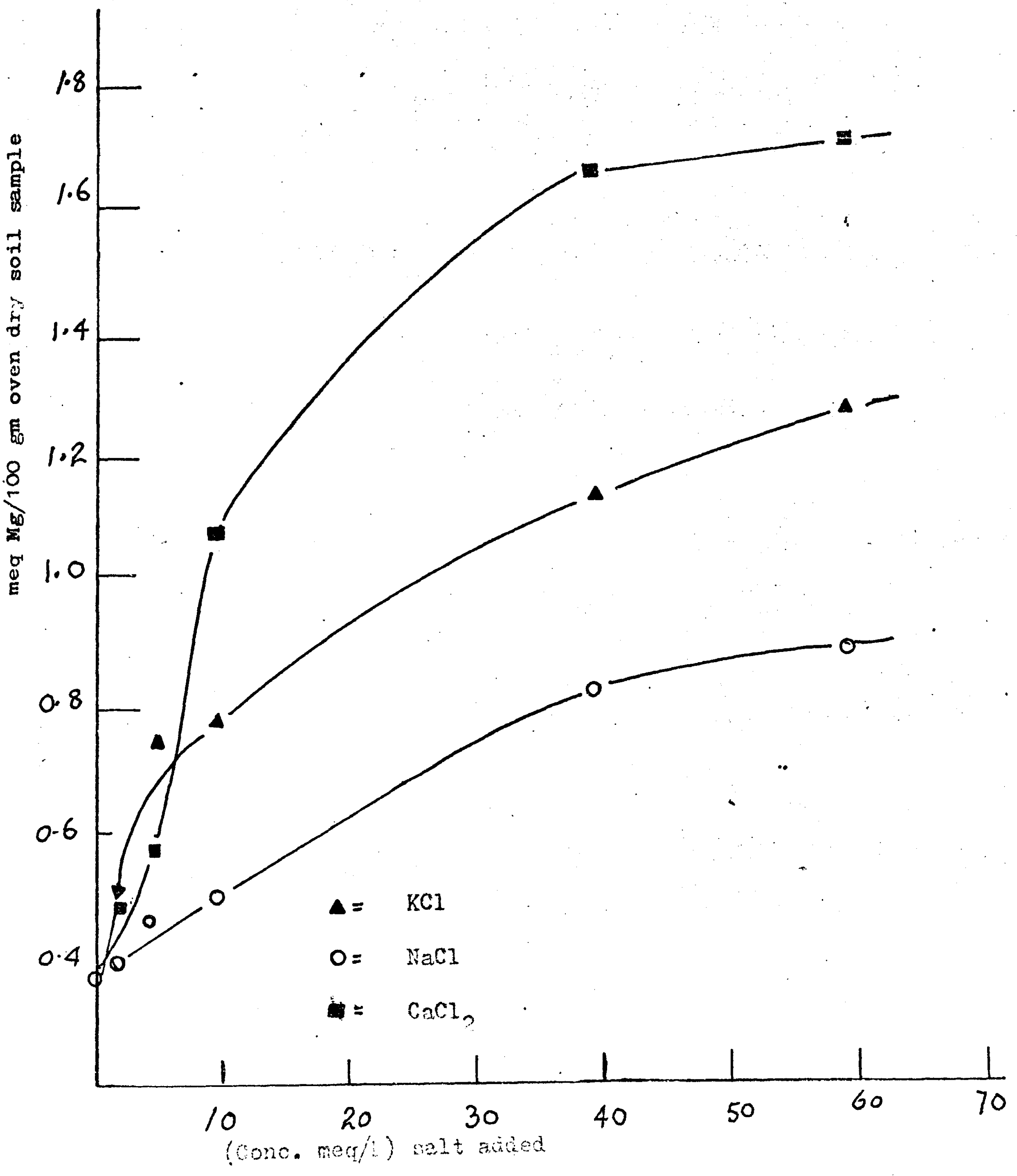


Fig. 1[illegible] The effect of salt on the [illegible]
[illegible] ([illegible] soil).

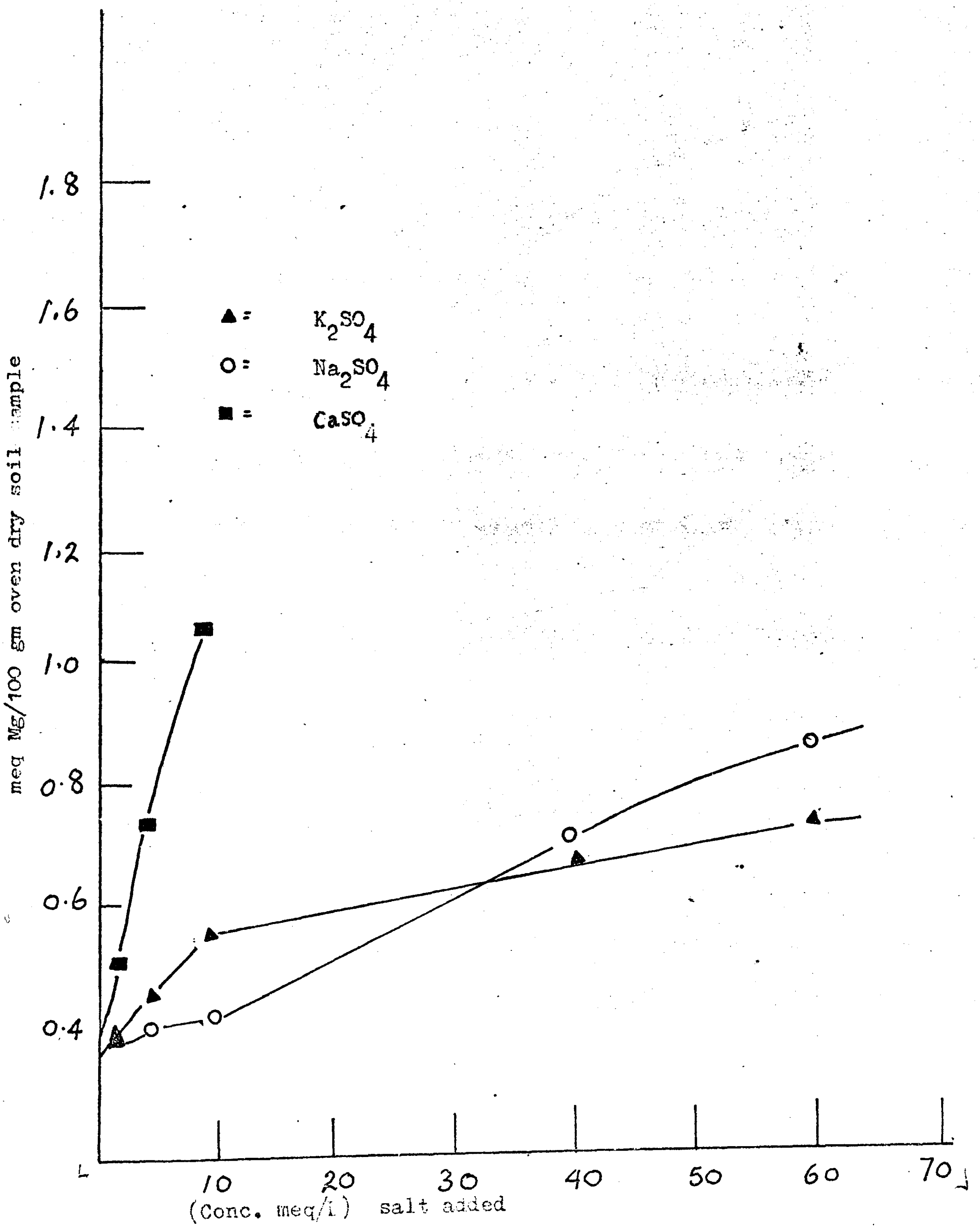


Fig. 12 The effect of salt on the displacement of native magnesium from the [illegible].

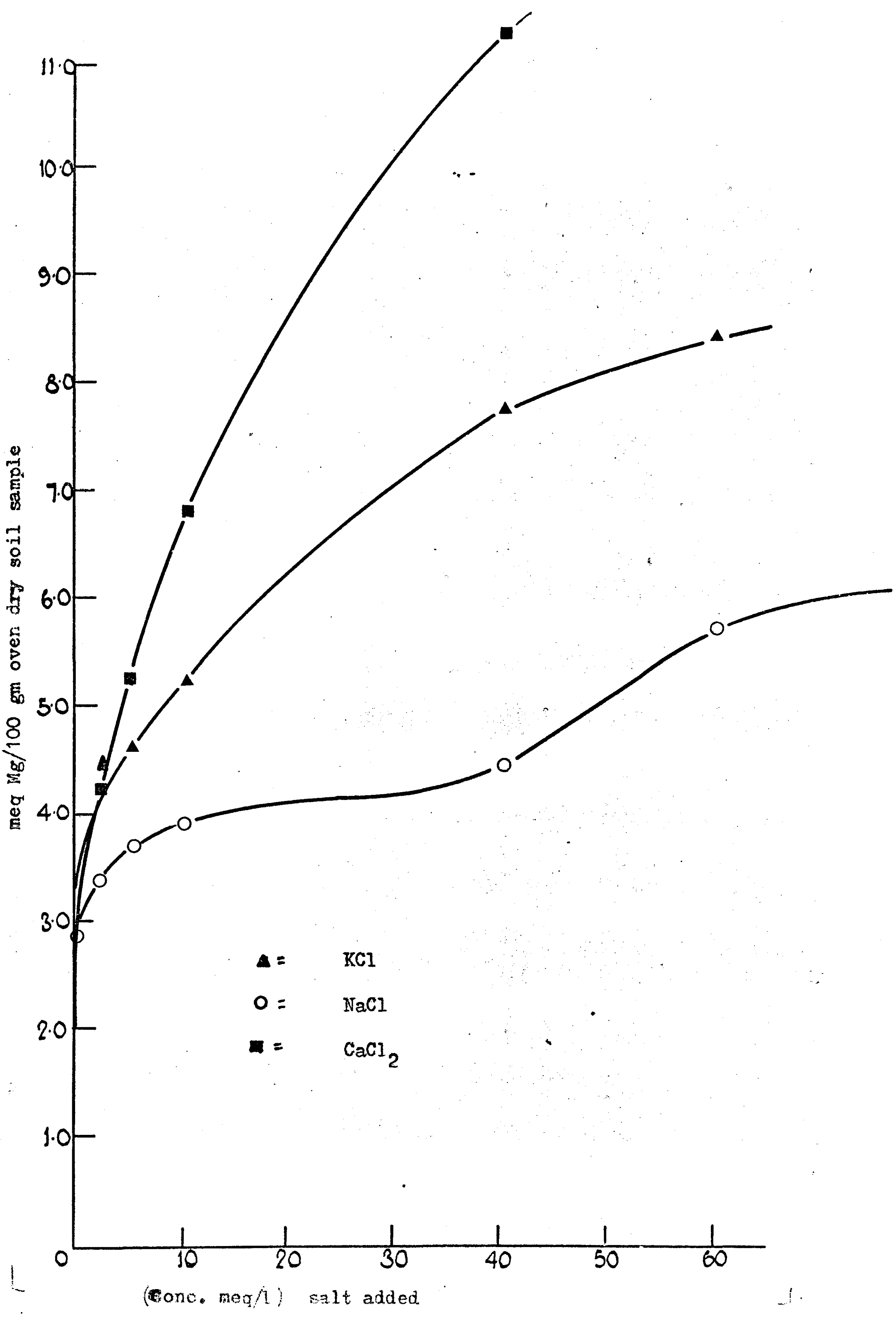


Fig. 13 The effect of salt to displacement of magnesium from the (GLEYED TOP SOIL).

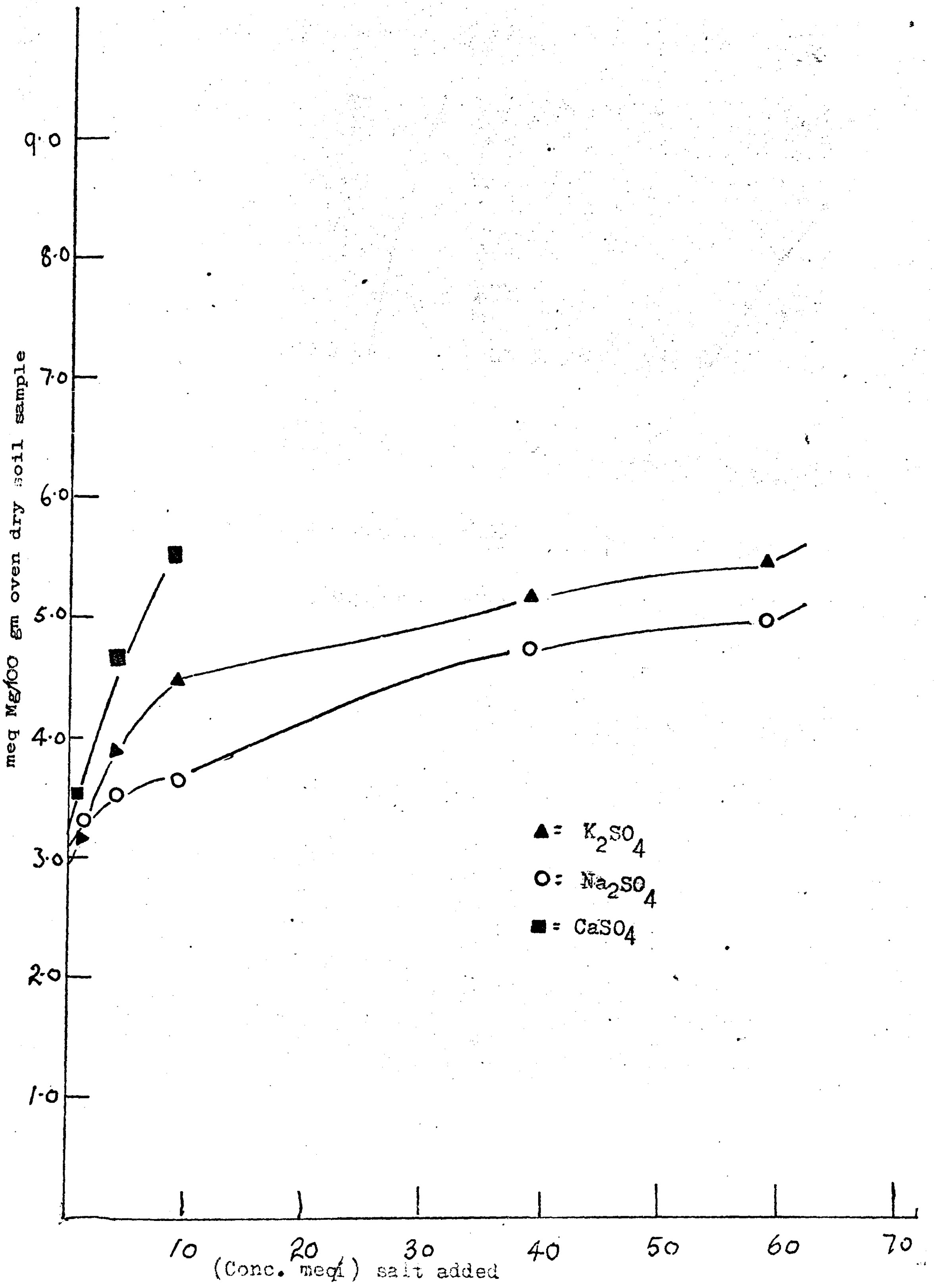


Fig. 14 The effect of salt to displacement of native magnesium from ([illegible]).

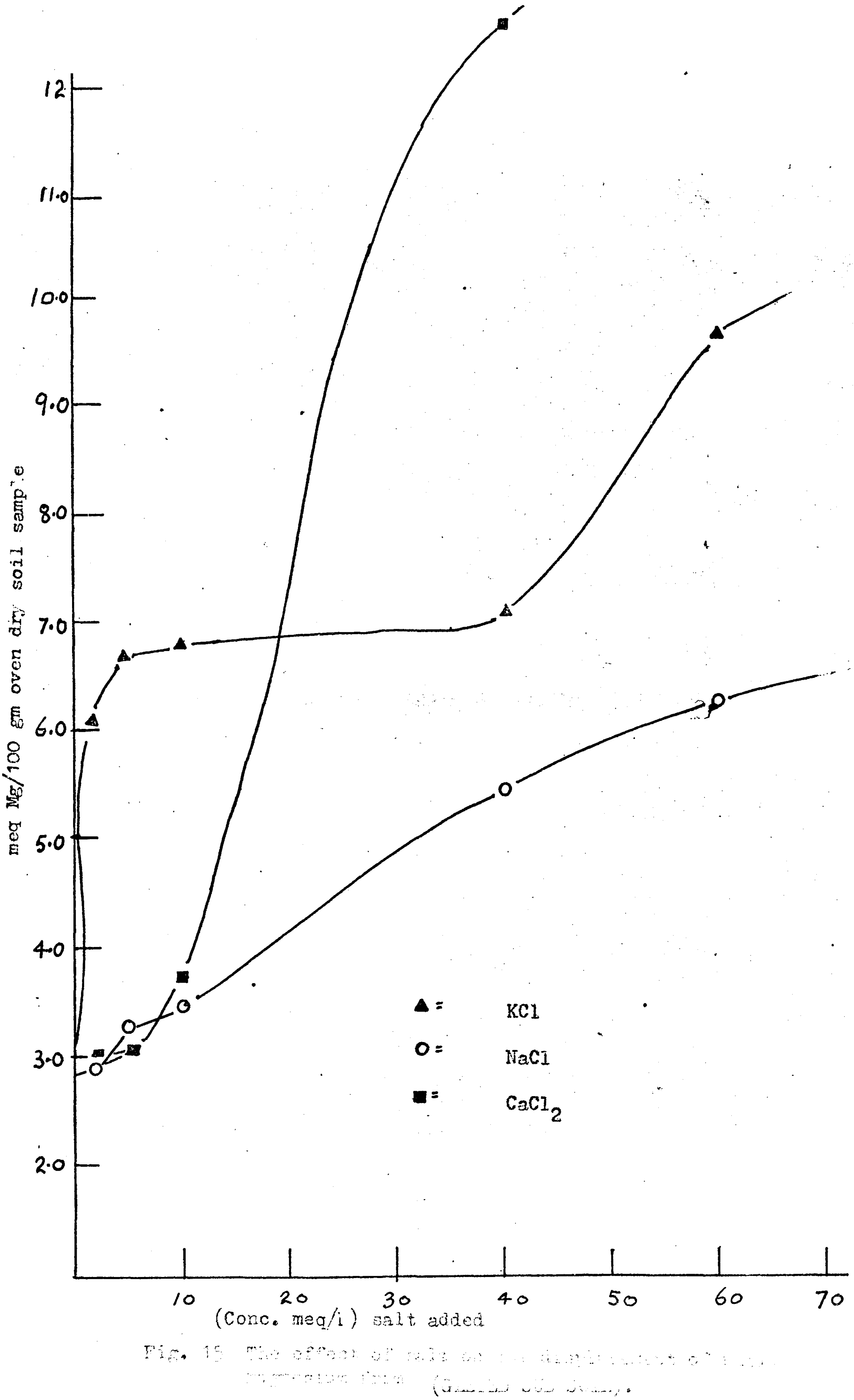


Fig. 15 The effect of salt on the displacement of [illegible] magnesium from (Gezira [illegible]).

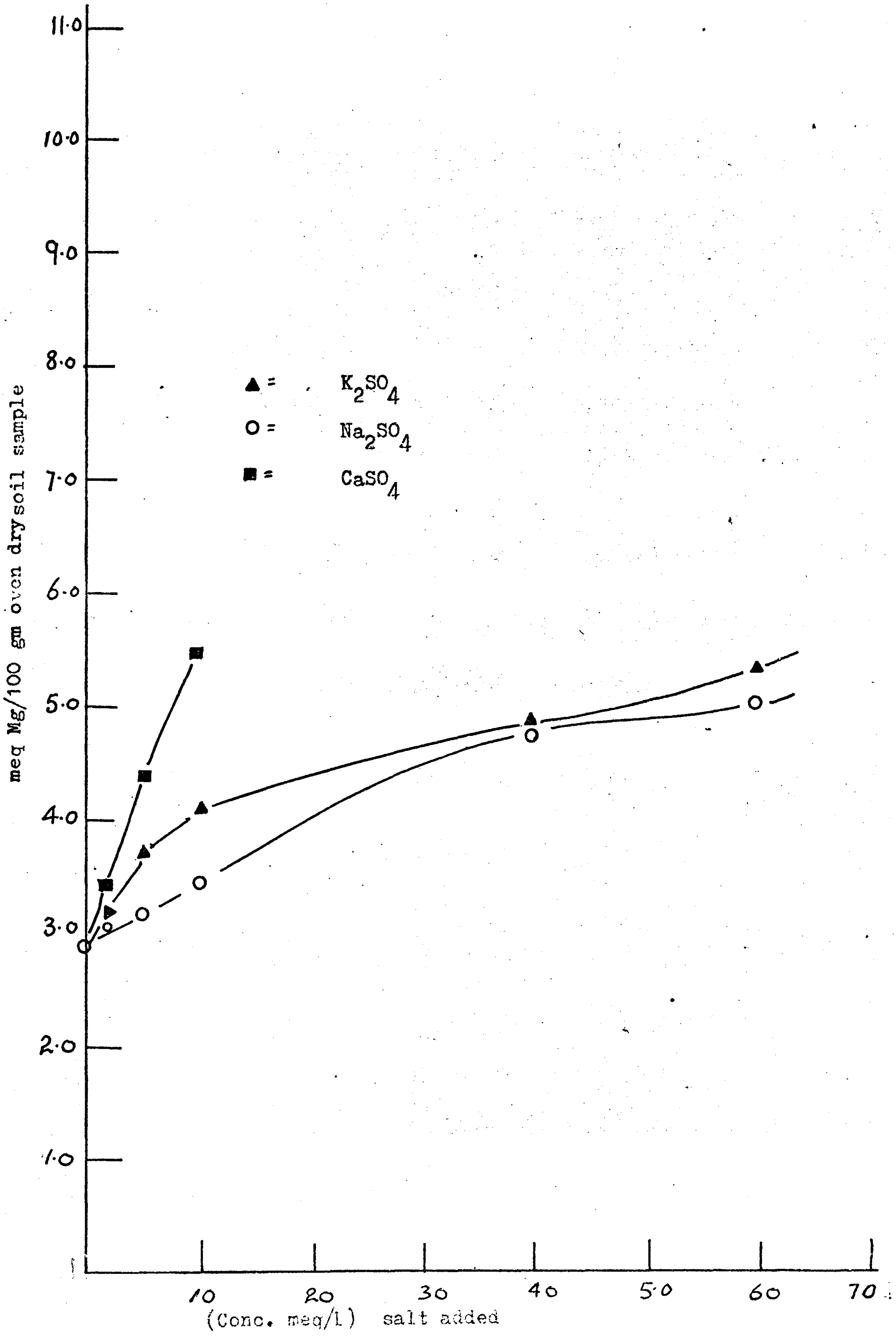


Fig. 16 The effect of salt on the displacement of native magnesium from the [illegible]

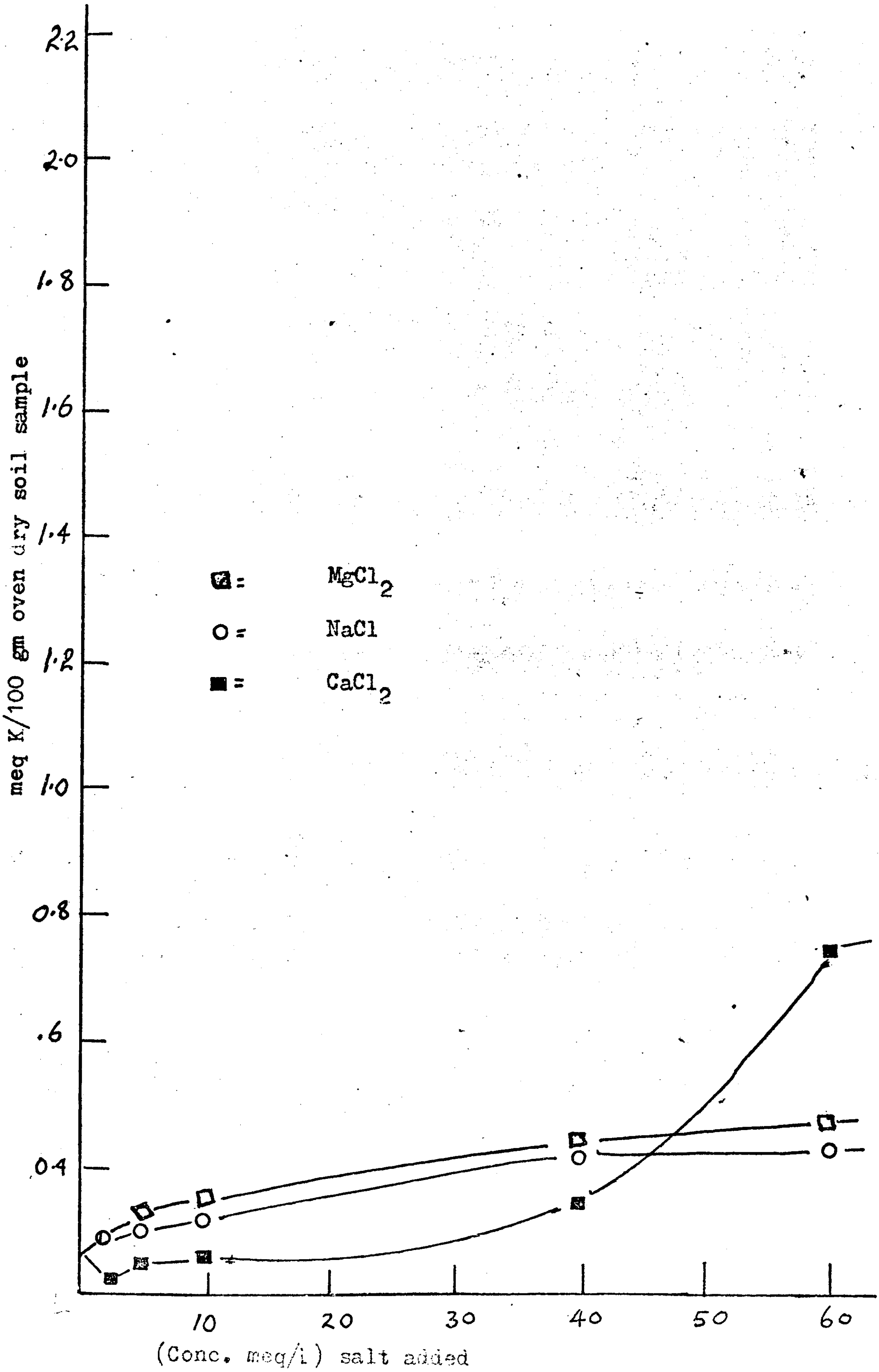


Fig. 17 The effect of salt on the displacement of native potassium [illegible]
[illegible]

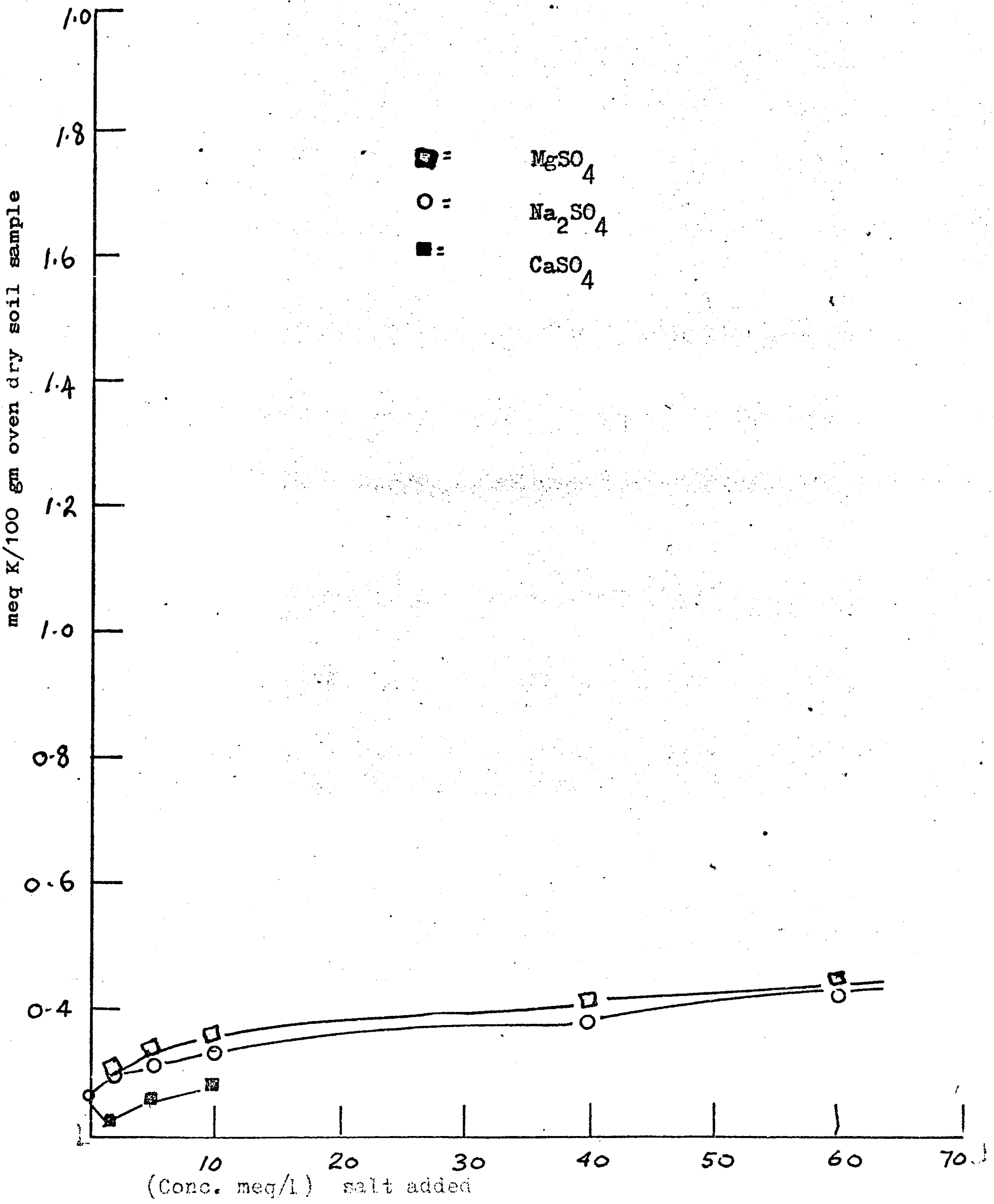


Fig. 18 The effect of salt on the displacement of native potassium
[illegible]

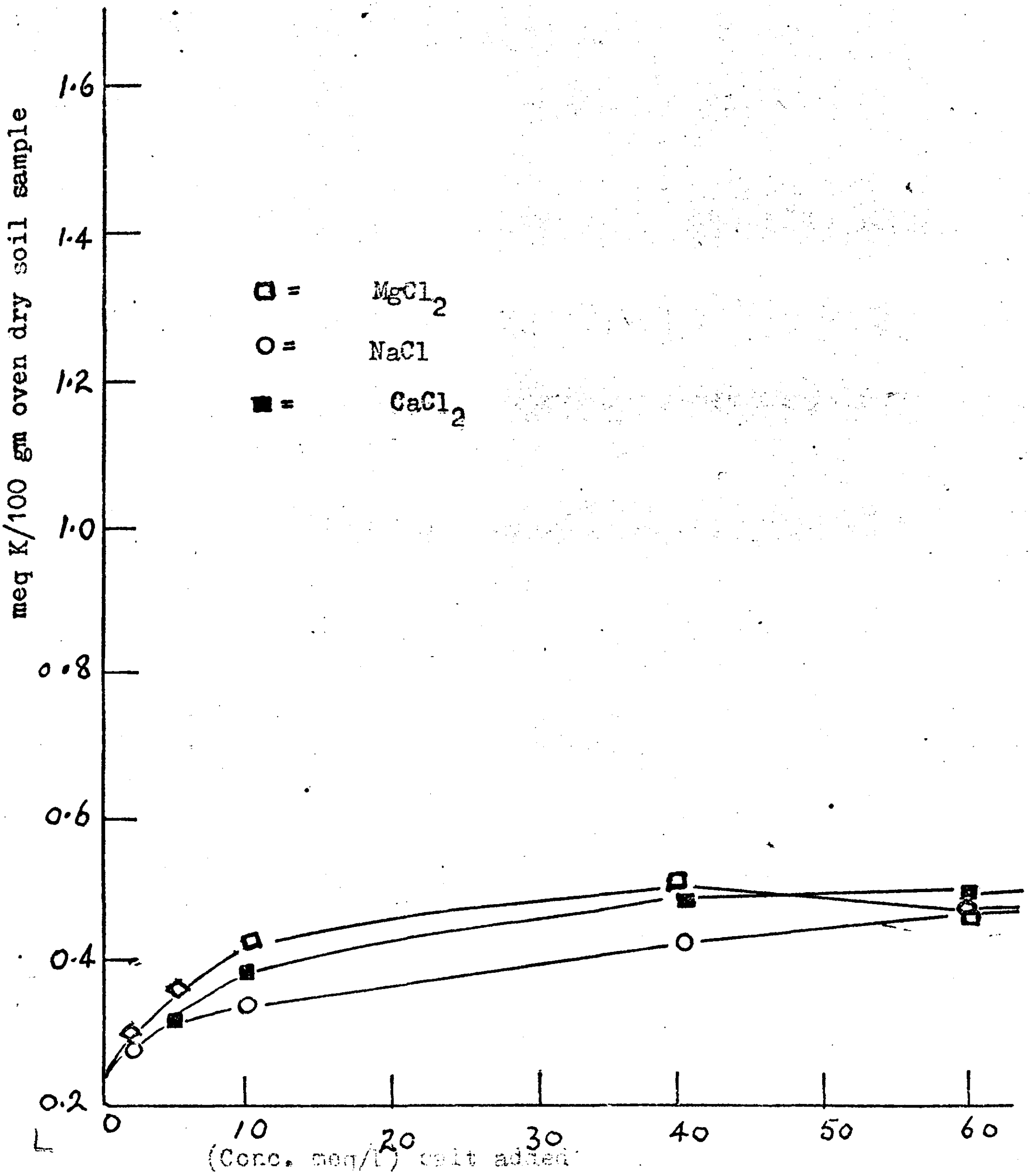


Fig. 19 The effect of salt on the displacement of native potassium from the (BROWN EARTH SUB SOIL).

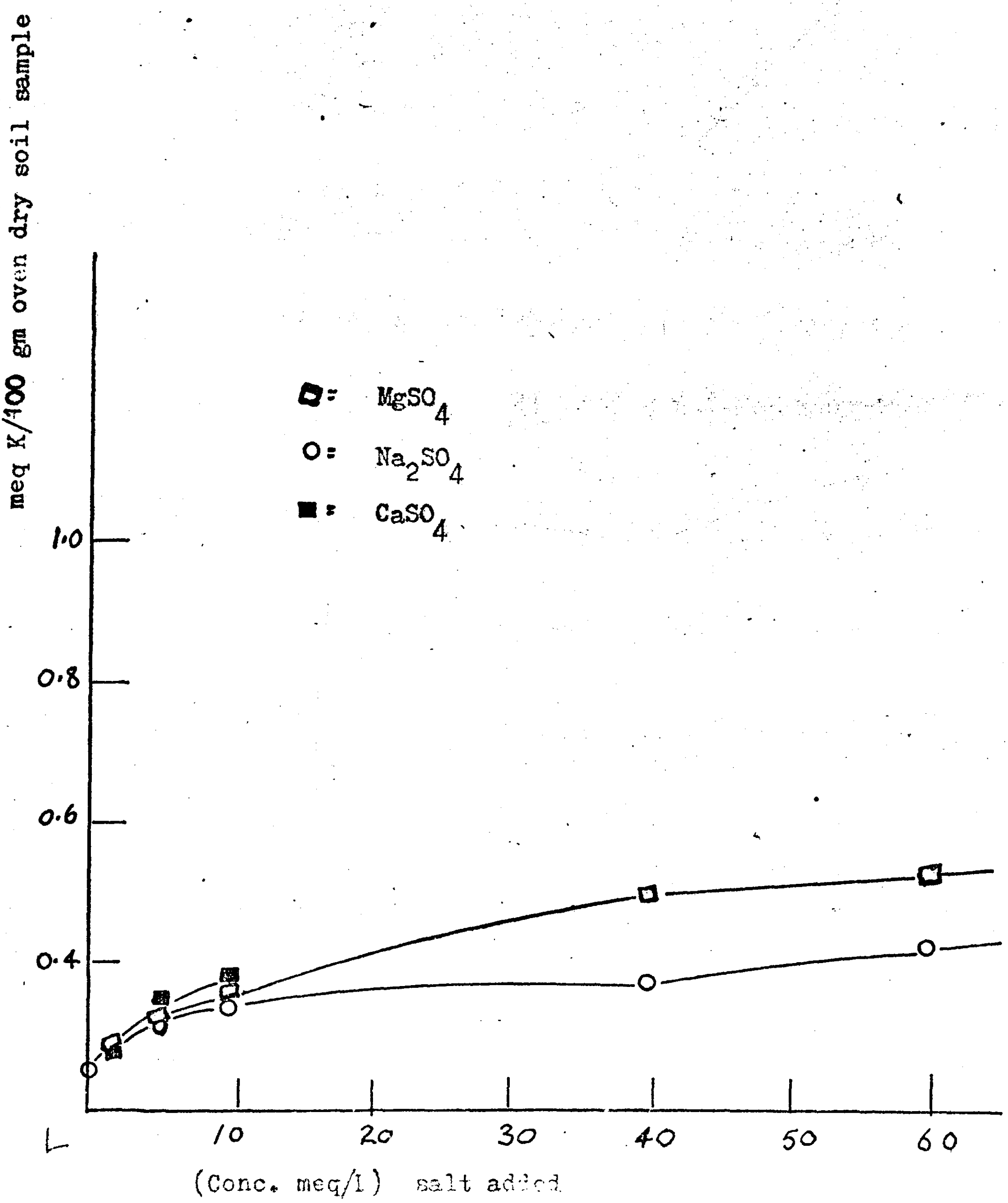


Fig. 20 The effect of salt on the displacement of native potassium from [illegible].

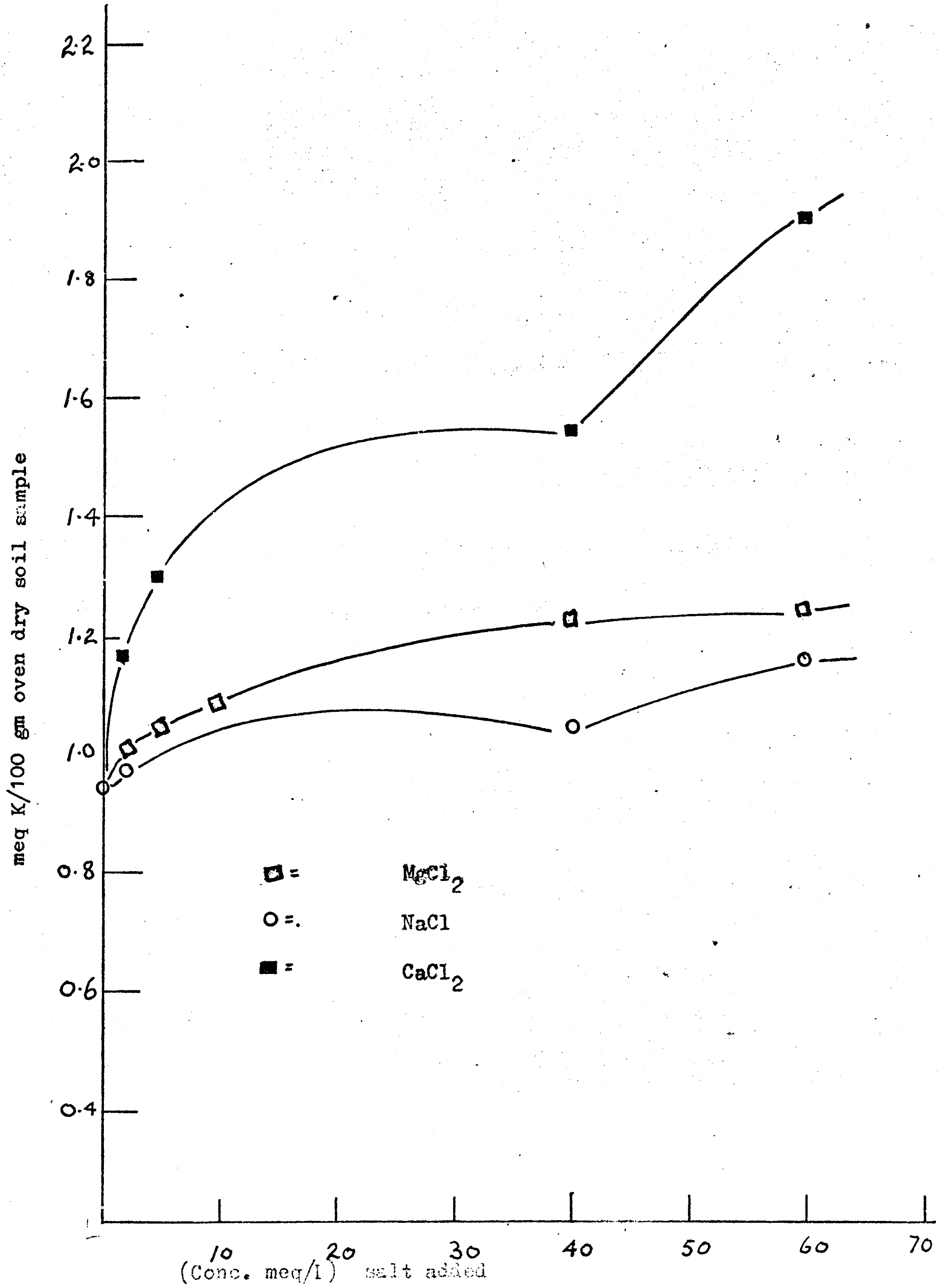


Fig. 21 The effect of salt on the displacement of native potassium from the ([illegible]).

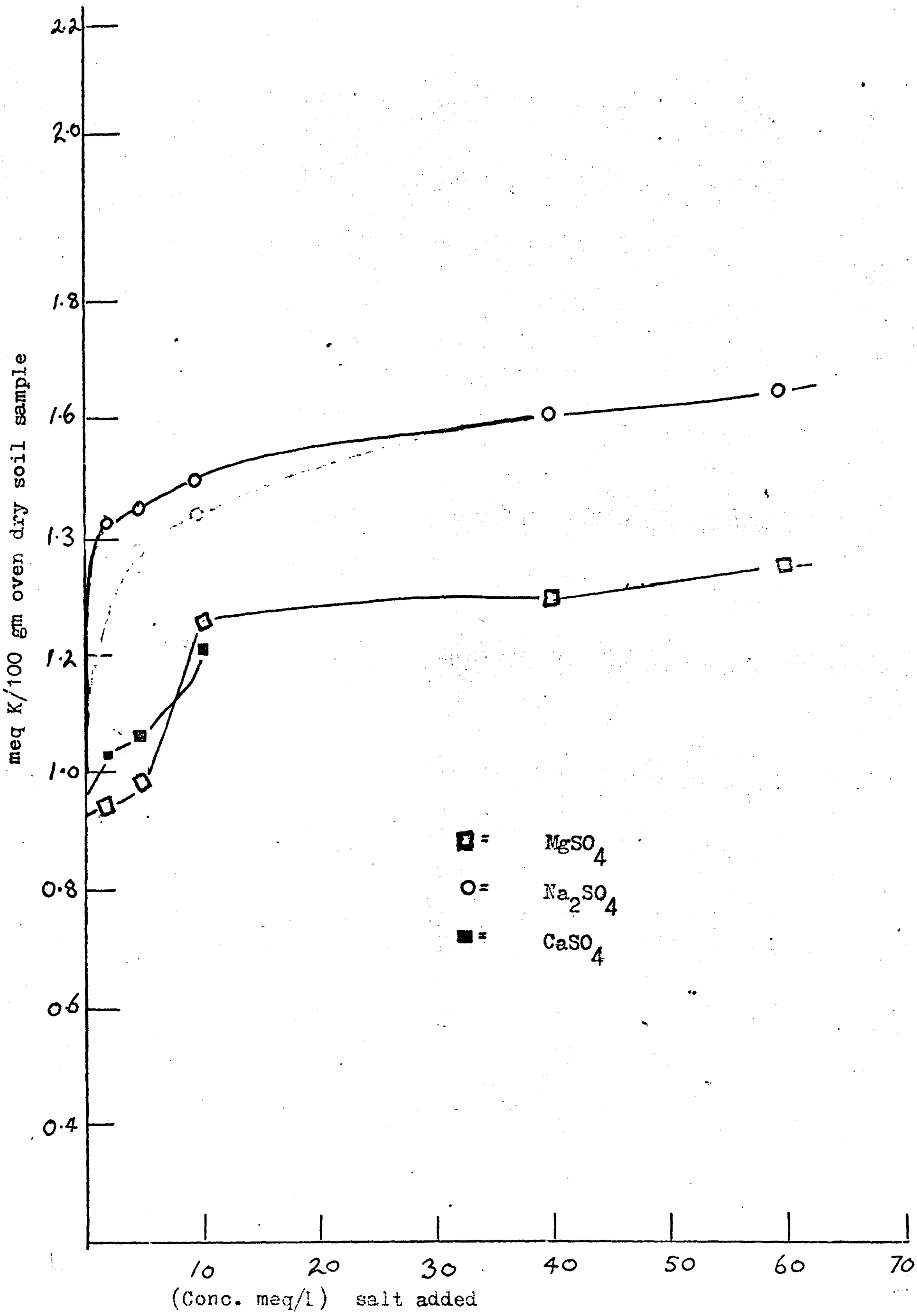


Fig. 22 The effect of salt on the displacement of potassium from the [illegible]

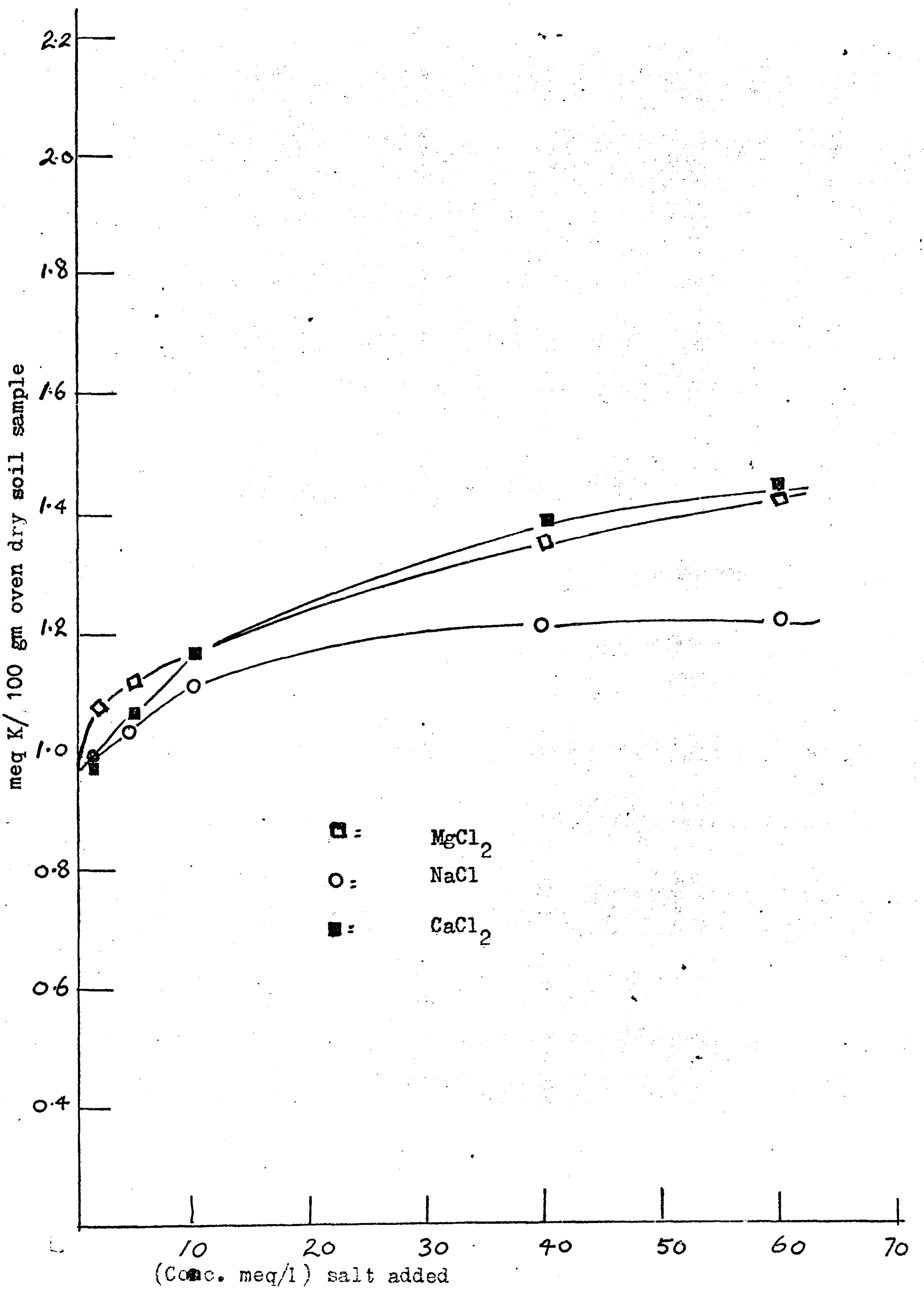


Fig. 23 The effect of salt on the displacement of native potassium from (GLEYED SUB SOIL).

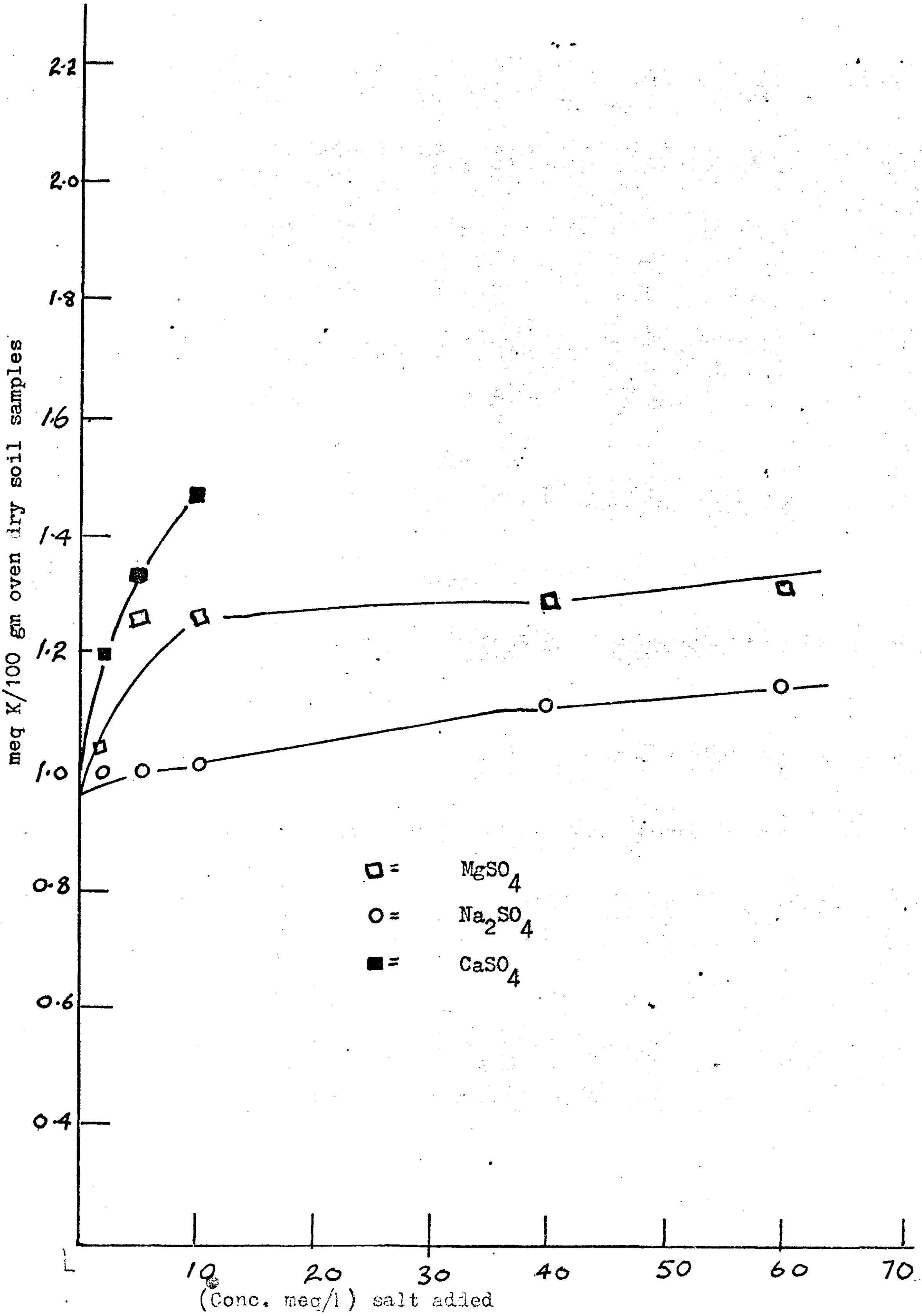


Fig. 24 The effect of salt on the displacement of native potassium from the (GLEYED SUB SOIL).

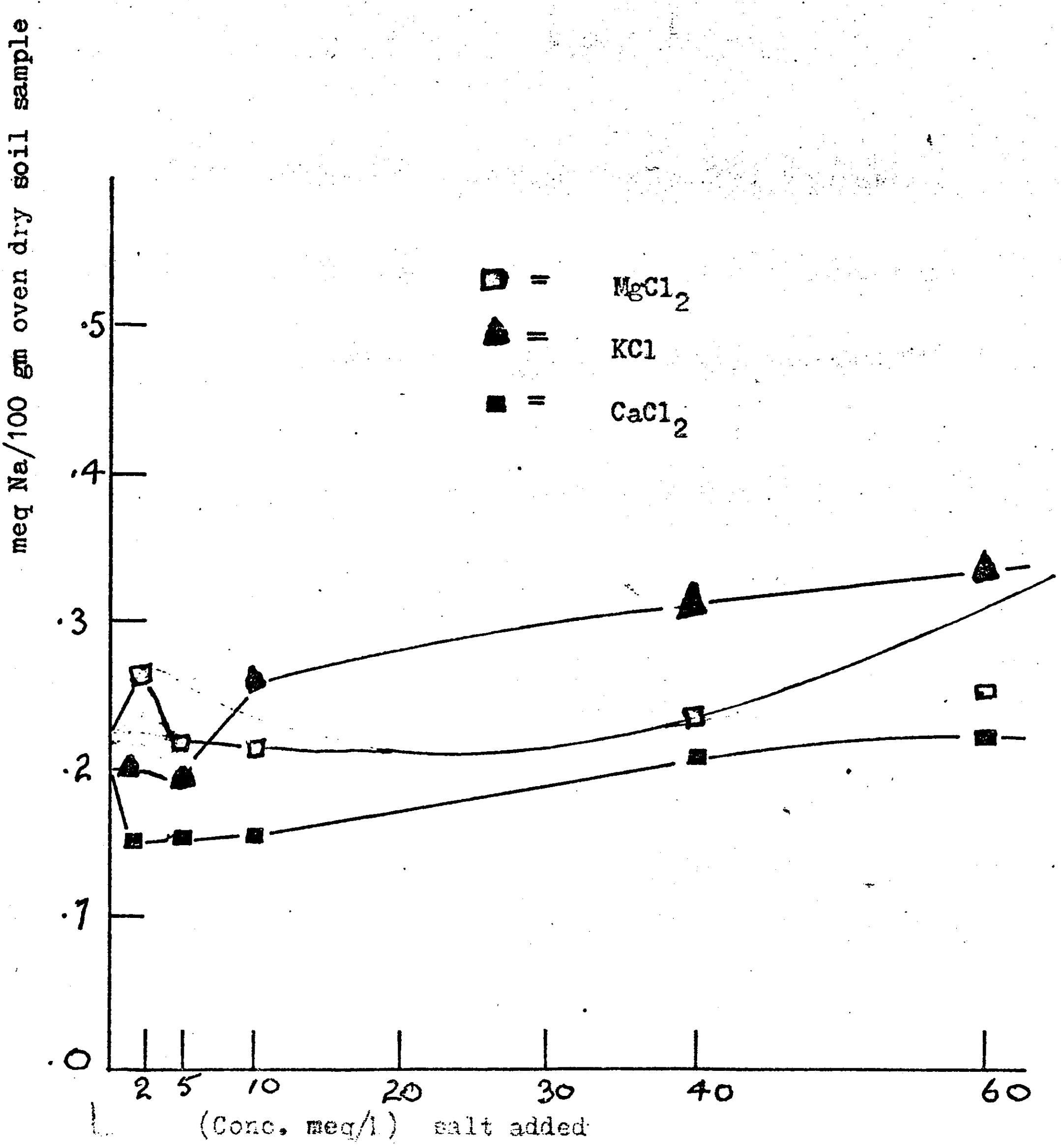


Fig. 25 The effect of salt on the displacement of native sodium from (BROWN EARTH TOP SOIL).

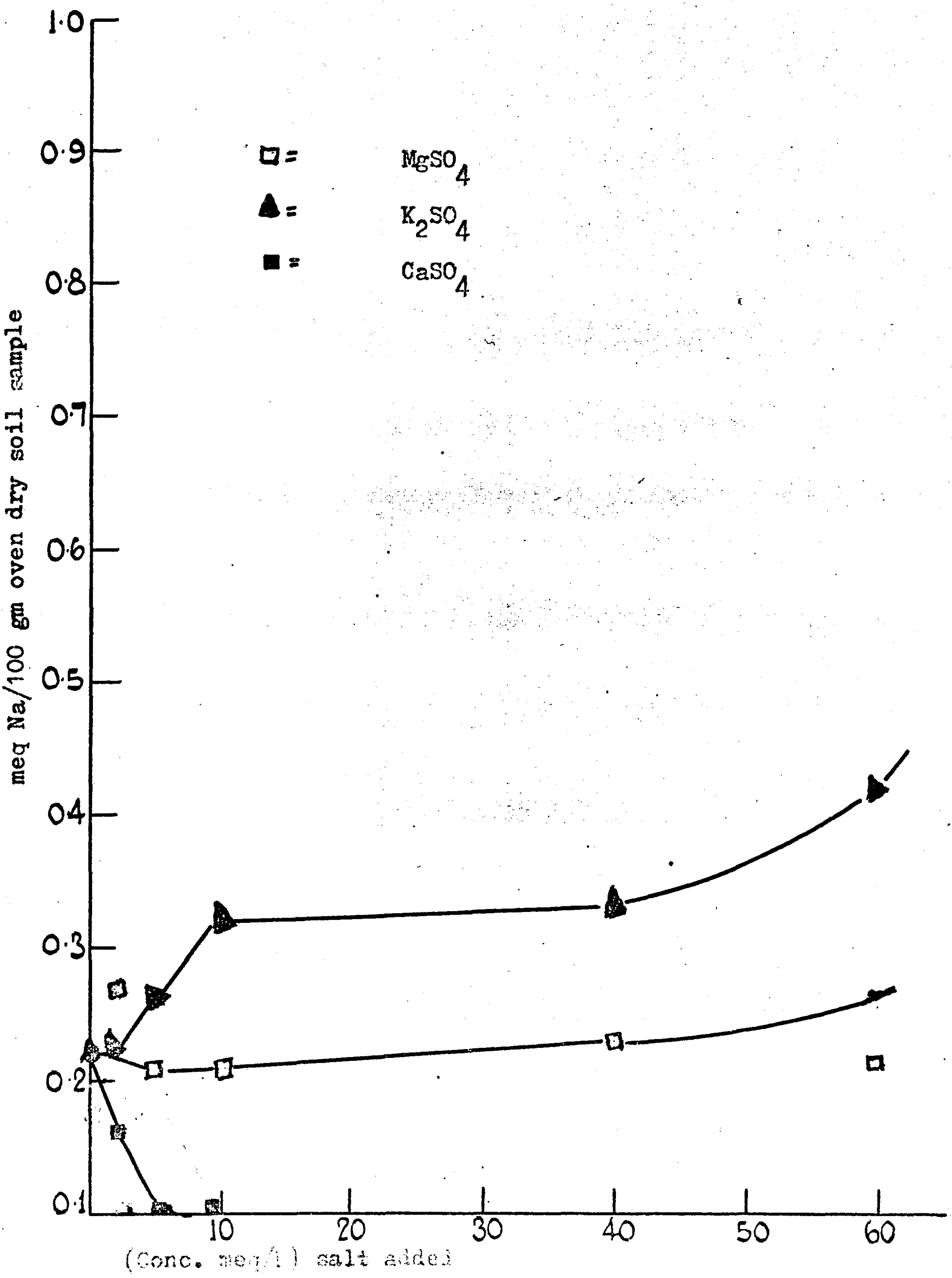


Fig. 26 The effect of adding salt on the [illegible] [illegible] from the (BROWN EARTH [illegible]

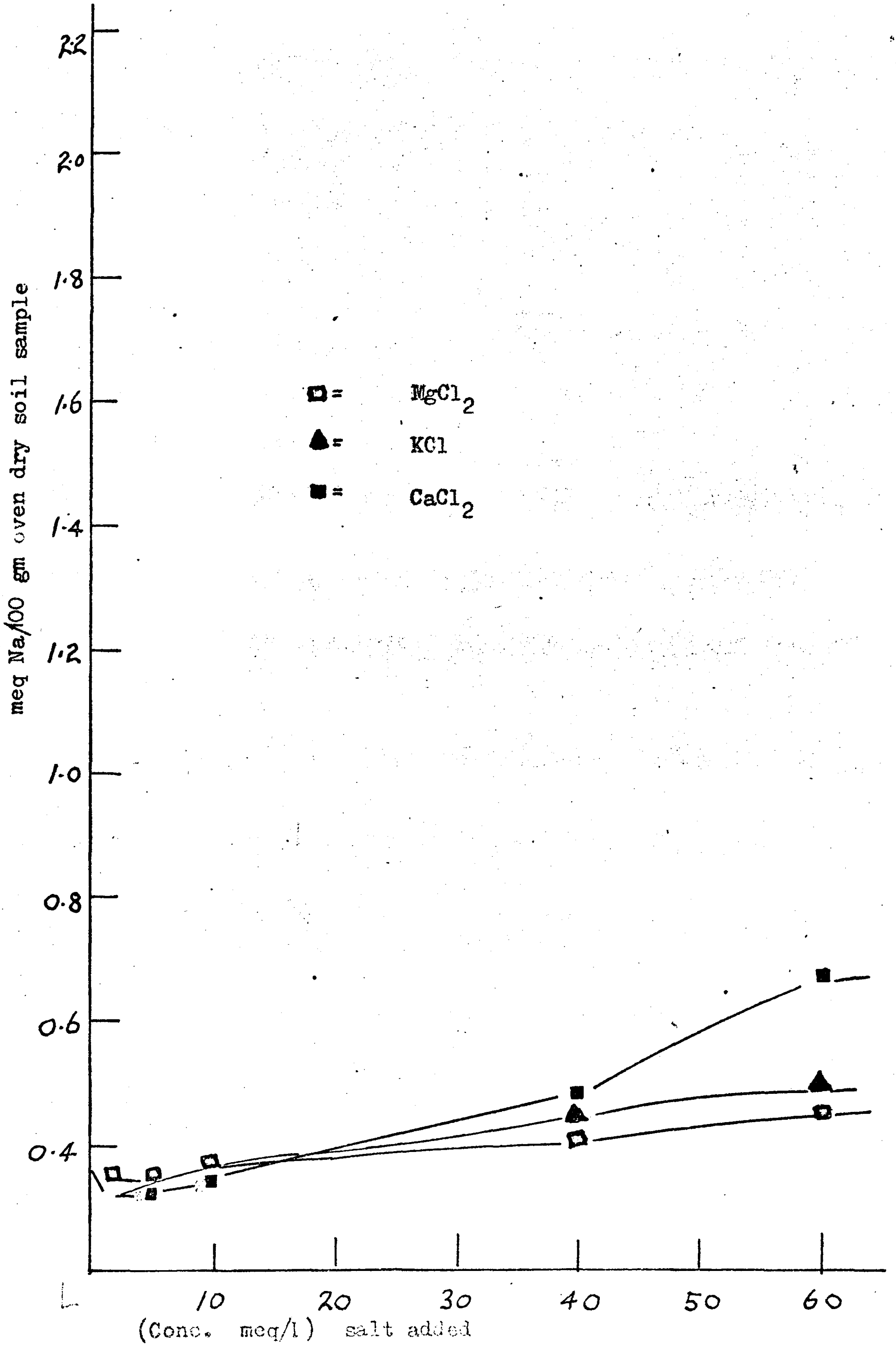


Fig. 27 The effect of salt on the displacement of native sodium [illegible]
([illegible]).

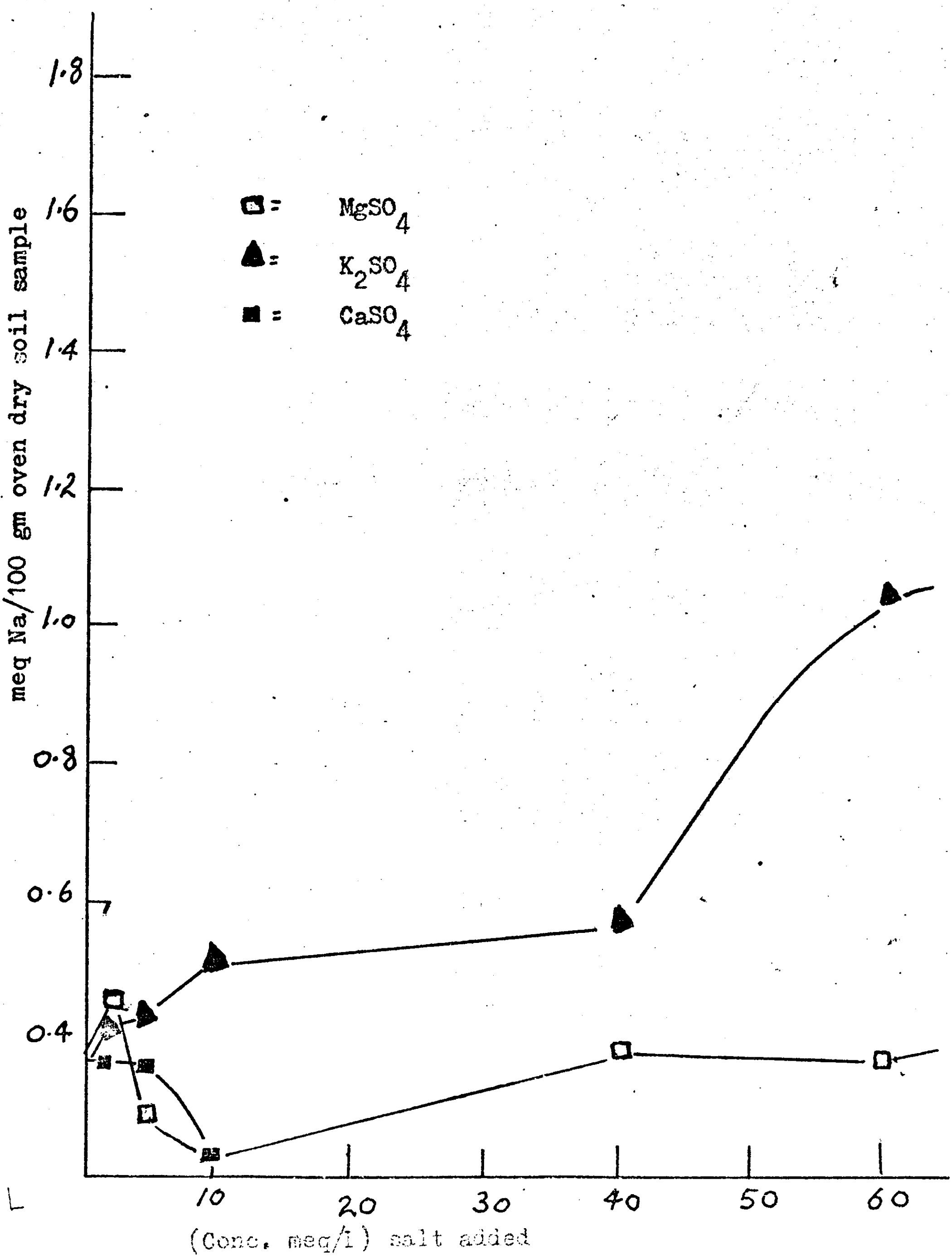


Fig. 2[illegible] The effect of [illegible] on the displacement of sodium [illegible] ([illegible]).

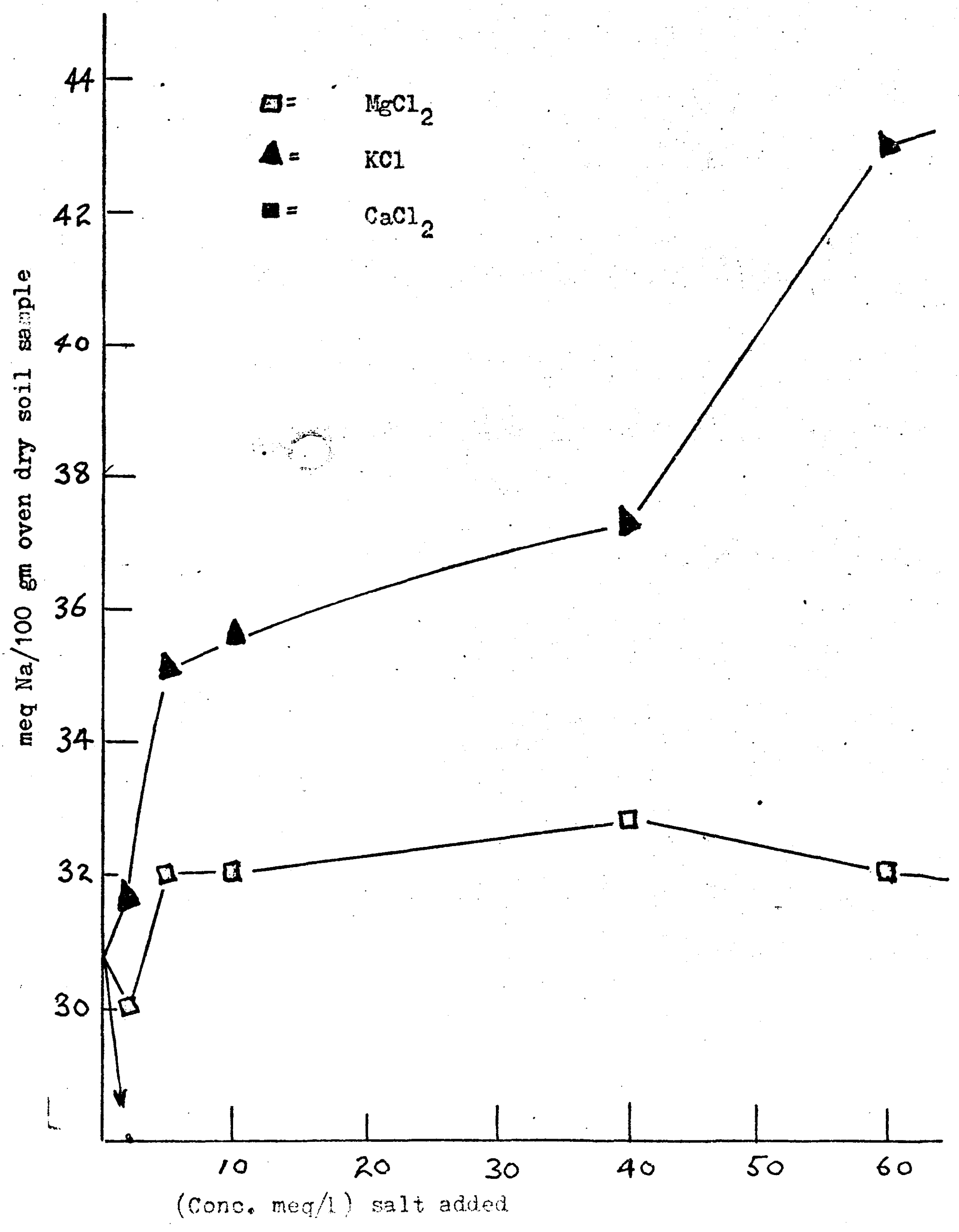


Fig. [illegible] The effect of [illegible]
(GLEYED TOP SOIL).

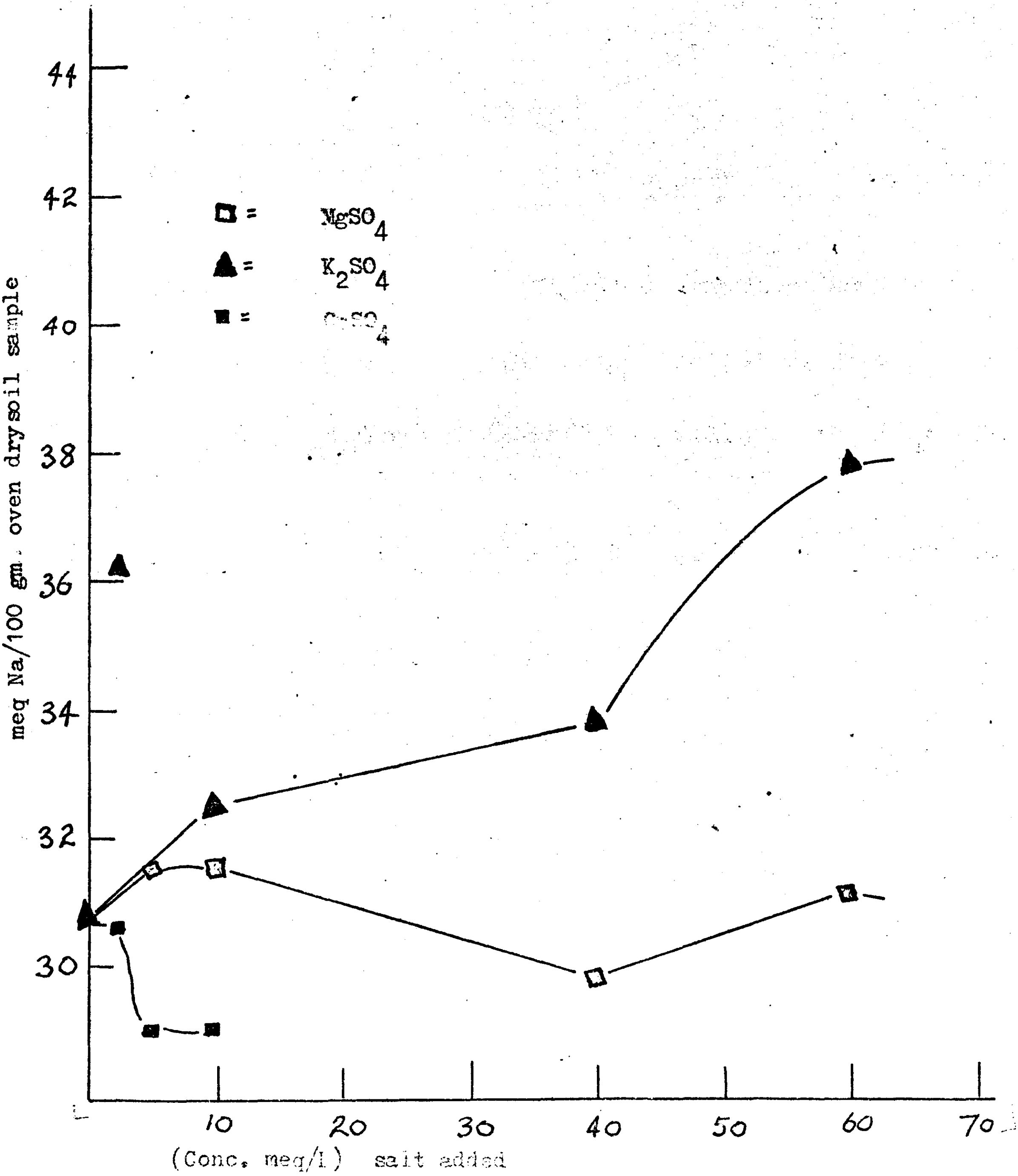


Fig. 30 The effect of [illegible]
(GEZIRA TOP SOIL).

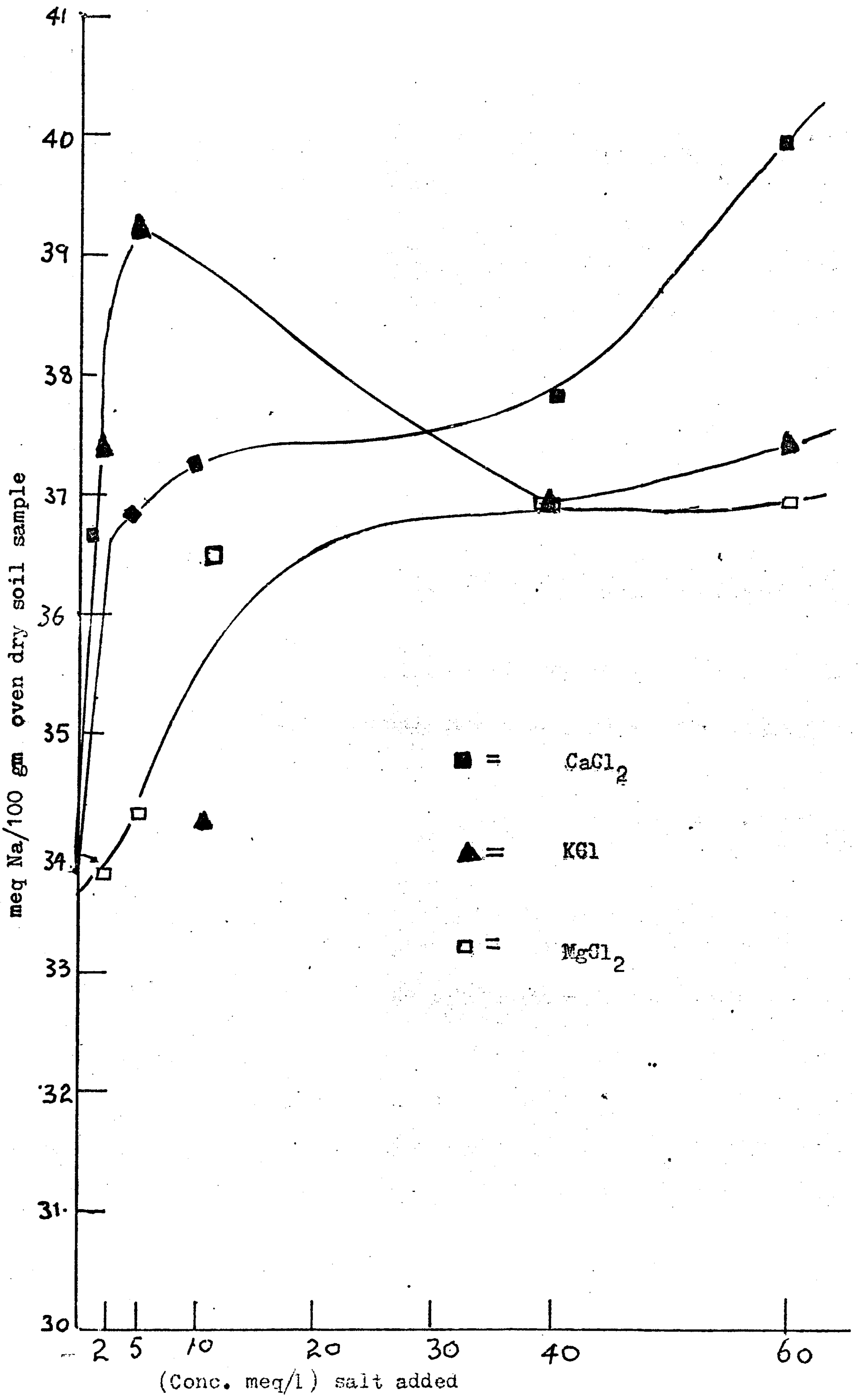


Fig. 31 The effect of salt on the displacement of native sodium from the ([illegible]).

APPENDIX

Conductivity measurements were made to estimate qualitatively the fraction of salt ionized.

The units employed for measuring the electrical conductivity of a soil solution (Whittles and Schofield-Palmer 1951) are :-

pS, pC, pN, pF when pC = pS

where S = ppm x 10^{-6} pC = pH + 1.17

C = mhos/cm pC = 5.74 - pF

N = Normality of solution

pF = 3 + Log 10 osmotic pressure in atmospheres.

Temperature control is important because of the rapid variation of the viscosity of water with temperature. The standard temperature for electrochemical measurements is 25°C. Usually the measurements are made at room temperature and suitably corrected. (Hesse 1971).

Conductivity measurements in the soil solution were taken to estimate the fraction of salt ionized in distilled water. Also measurements were made in the presence of soil and with soil treated with $CaCO_3$ covering a wide range of concentrations, as shown in Table (6.1) A and B.

The addition of monovalent cations was found to increase the conductivity more than divalent cations, which indicates that monovalent cations have a greater effect on soil salinity and Cl salts more than SO_4, as shown in Table (6.1 A).

$CaSO_4$ in soil reduced the conductivity of solutions of divalent cations, probably by interacting with the ions and reducing their mobility. Less effect was noted with unibivalent salts($CaCl_2$, $MgCl_2$) and no effect with uni-univalent salts (NaCl, KCl).

The presence of $CaCO_3$ in soil increased the conductivity of the salt solution, as shown in Tables(6.2) and (6.3) except in the case of K_2SO_4 and $MgCl_2$.

The effect of low concentrations of salts up to 10 meq/l had proportionally a greater effect than the addition of higher concentrations - 40-80 meq/l, as presented in graphical form (32,33,34).

This may be related to the solubility of salts, and the formation of ion pairs which effect the mobility of ions at higher concentrations.

It was found in all cases that top soil had a higher conductivity than sub soil. The addition of salt increased the conductivity in top soil slightly more than sub soil.

It was found that salts increase the conductivity of soil extracts in brown earth top soil in the following order :-

For SO_4 : K > Na > Ca > Mg
For Cl : K > Na > Mg > Ca

But in brown earth sub soil the order was :-

K > Na > Ca > Mg for SO_4 and
Na > K > Mg > Ca for Cl

In the presence of $CaSO_4$ the conductivity of brown earth(top and sub) soil was decreased to the same extent, as shown (32,33 and 34) and in Tables (6.2)and (6.3).

In the presence of lime the decrease was the same with SO_4 but with Cl the effect was greater with top soil than with sub soil.

It was found that in brown earth top soil the order of conductivity was :-

K > Na > Mg for Cl and
Na > K > Mg for SO_4
} as shown in Table (6.2)

In sub soil the order was :-

K > Na > Mg for Cl and
Na > Mg > K for SO_4.
} as shown in Table (6.3)

It was concluded that the addition of monovalent and divalent salts to the soil increases its electrical conductivity.

The addition of monovalent salt was found to increase the conductivity more than divalent. This indicated that monovalent salts have the more important effect on salt salinity.

However, the kind and amount of ions (Na, K, Mg, Ca) present in soluble forms produces high salinity which is shown by high conductivity.

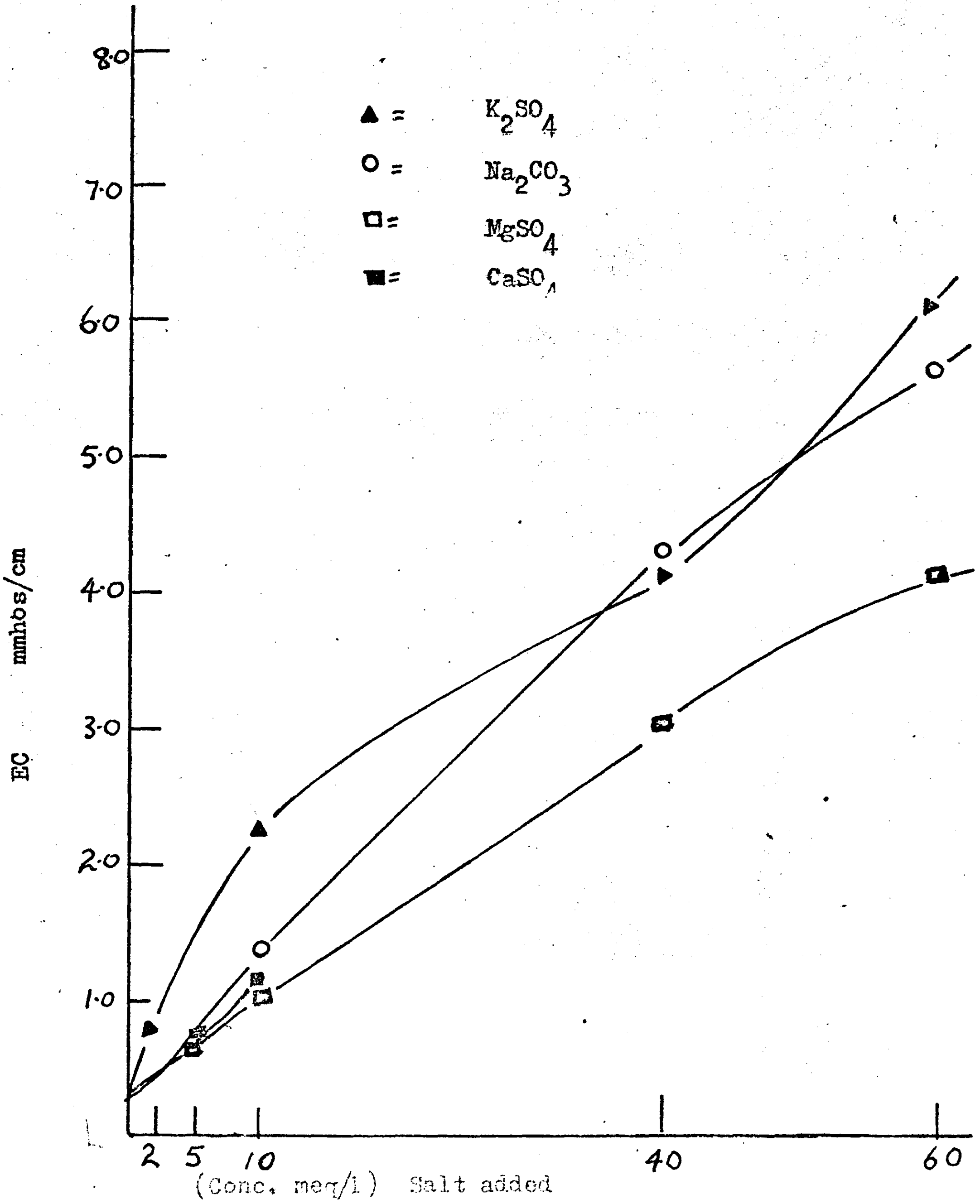


Fig. 32. The effect of salt on conductivity of soil extract, (BROWN EARTH TOP SOIL).

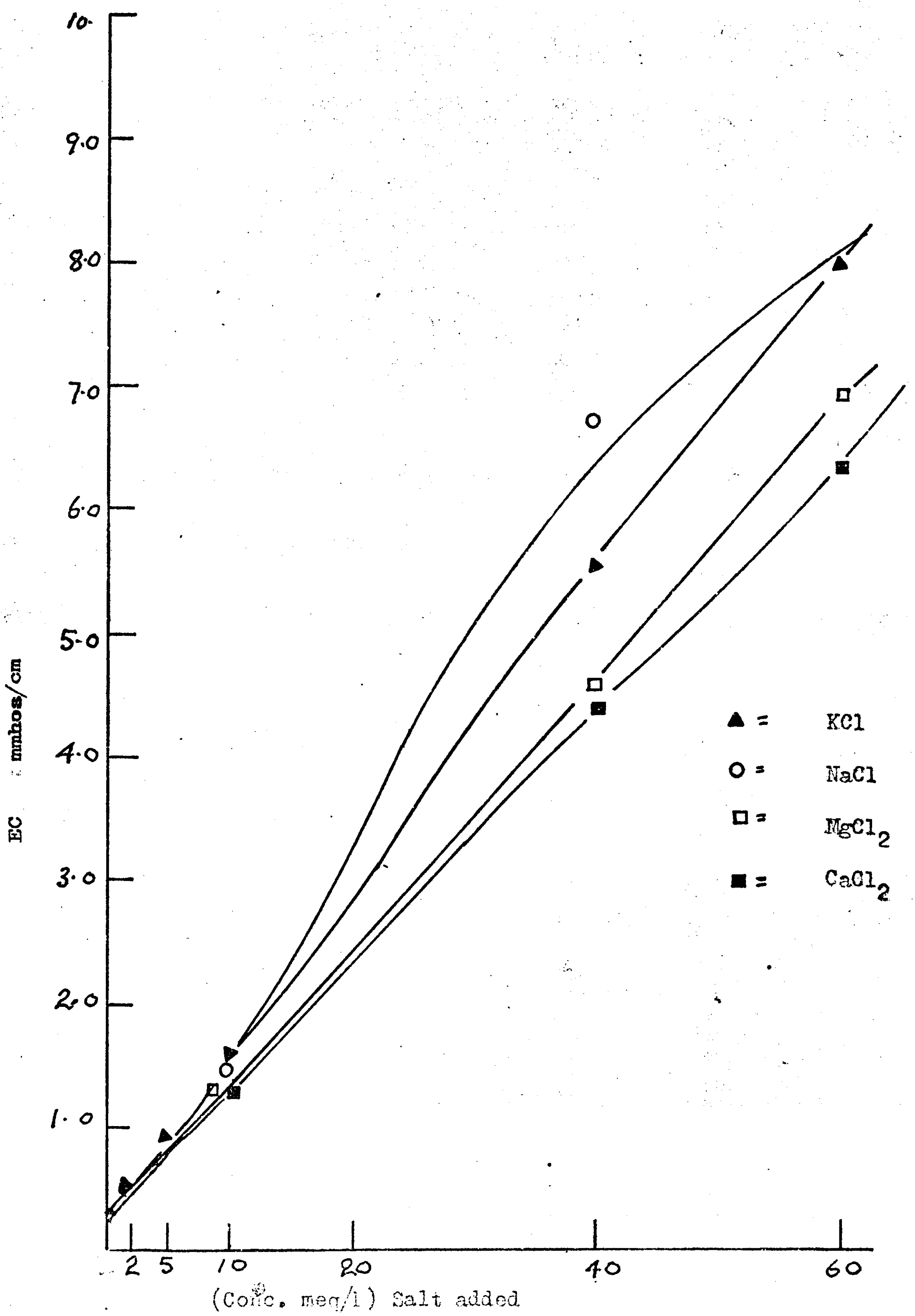


Fig. 33. The effect of salt on conductivity of soil extract, (BROWN EARTH TOP SOIL).

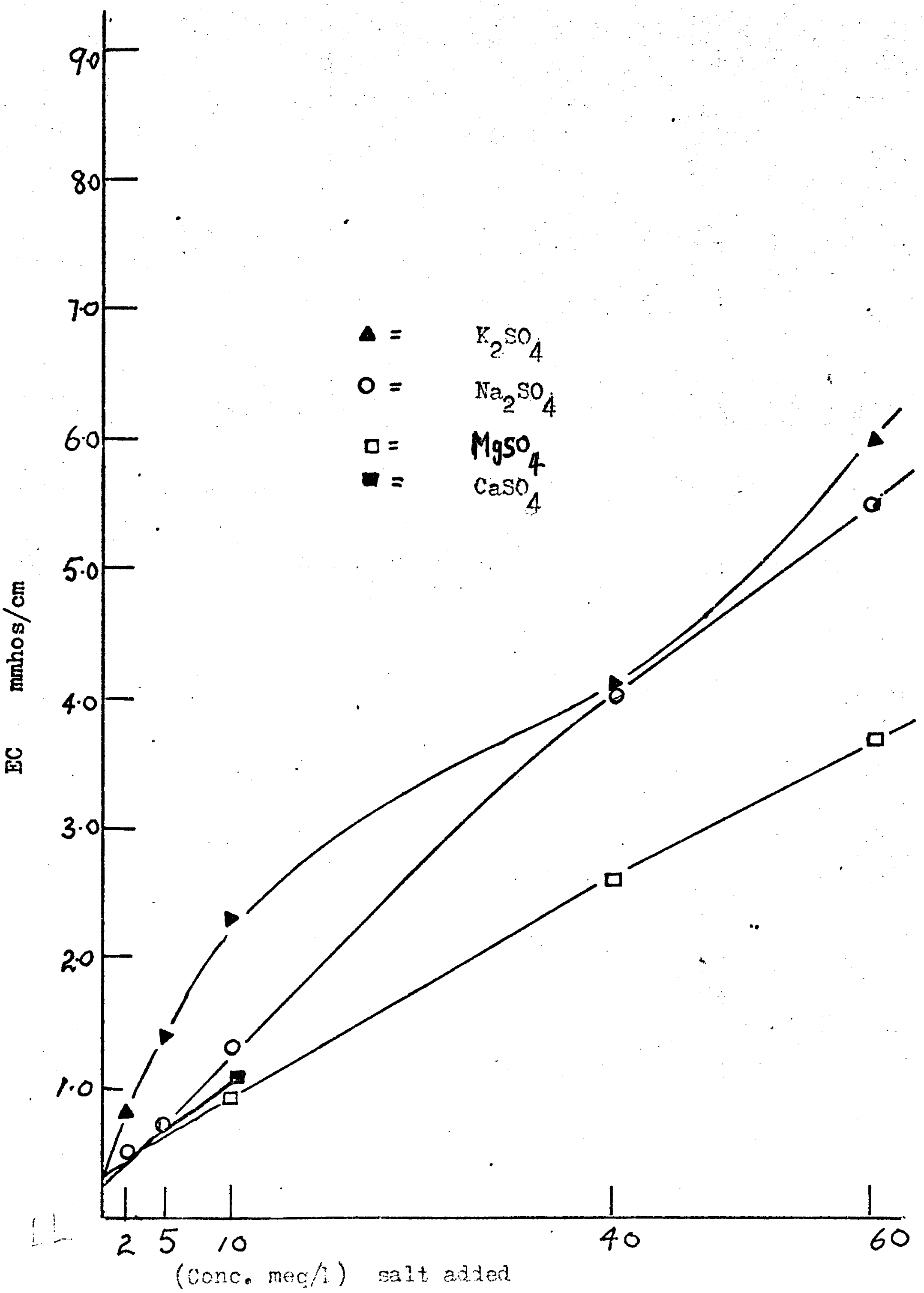


Fig. 34. The effect of salt on the conductivity of soil extract,

([illegible] soil).

Table (6.1)

Determination of conductivity with different concentrations of salt in distilled water

A mmhos/cm

	In absence of lime ($CaCO_3$)							
Conc. Meq/L	NaCl	Na_2SO_4	KCl	K_2SO_4	$MgCl_2$	$MgSO_4$	$CaCl_2$	$CaSO_4$
0	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
2	0.27	0.25	0.30	0.76	0.27	0.24	0.30	0.27
5	0.66	0.55	0.72	1.41	0.73	0.52	0.69	0.62
10	1.28	1.1	1.4	2.61	1.32	0.89	1.33	0.28
40	4.89	3.8	5.0	4.78	4.25	2.67	4.65	nd
60	6.90	5.2	7.0	6.96	6.58	3.79	6.90	nd
80	9.45	7.0	10.0	8.70	8.38	4.91	8.82	nd

B mmhos/cm

In presence of 0.1 gm $CaCO_3$			In presence of 1.0 gm $CaCO_3$	
NaCl	$MgCl_2$	NaCl + $MgCl_2$	NaCl	$MgCl_2$
0.17	0.17	nd	0.18	0.18
0.36	0.71	nd	0.36	0.38
0.64	1.37	nd	0.66	0.68
1.49	2.76	2.68	1.43	1.61
5.23	5.42	9.16	3.25	5.35
7.37	8.92	nd	6.18	6.24
10.11	10.11	nd	9.51	8.92
11.89	11.89	nd	11.89	10.70

nd = not determined

mmhos/cm = millimhos/cm

Table (6.2)

Determination conductivity of soil extract (mmhos/cm) Brown earth top soil 1:10 soil water ratio

	In absence of lime and gypsum								In presence of gypsum (10 meq/L)						In presence lime 1 gm CaCo$_3$					
meq/L salt	NaCl	Na$_2$SO$_4$	KCl	K$_2$SO$_4$	MgCl$_2$	MgSO$_4$	CaCl$_2$	CaSO$_4$	NaCl	NaSO$_4$	KCl	K$_2$SO$_4$	MgCl$_2$	MgSO$_4$	NaCl	Na$_2$SO$_4$	KCl	K$_2$SO$_4$	MgCl$_2$	MgSO$_4$
0	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	1.28	1.28	1.28	1.28	1.28	1.28	0.31	0.31	0.31	0.31	0.31	0.31
2	0.54	0.54	0.54	0.82	0.52	0.46	0.50	0.45	1.53	1.42	1.53	1.47	1.34	1.30	nd	nd	nd	nd	nd	nd
5	0.91	0.61	0.94	1.33	0.90	0.72	0.83	0.72	1.92	1.79	1.92	1.79	1.48	1.41	nd	nd	nd	nd	nd	nd
10	1.51	1.36	1.57	2.29	1.44	1.11	1.32	1.1	2.55	2.3	2.81	2.43	1.79	1.66	1.75	1.56	1.93	1.99	0.97	1.37
40	6.67	4.25	5.55	4.10	4.61	3.07	4.37	nd	nd	nd	nd	nd	nd	nd	6.86	5.74	7.98	4.24	3.37	4.12
60	7.12	5.59	7.99	6.14	6.91	4.10	6.33	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
80	9.84	7.6	10.53	8.20	8.53	4.10	8.50	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

Table (6.3)

Determination conducitivy of soil extract (mmhos/cm) Brown earth sub soil 1:10 soil water ratio

Conc.	In absence of lime and gypsum								In presence gypsum gm CaSo$_4$ = 10 meq/L						In presence lime 1 gm CaCo$_3$ = 20 meq/L					
meq/L salt	NaCl	Na$_2$SO$_4$	KCl	K$_2$SO$_4$	MgCl$_2$	MgSO$_4$	CaCl$_2$	CaSO$_4$	NaCl	NaSO$_4$	KCl	K$_2$SO$_4$	MgCl$_2$	MgSO$_4$	NaCl	Na$_2$SO$_4$	KCl	K$_2$SO$_4$	MgCl$_2$	MgSO$_4$
0	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29	1.28	1.28	1.28	1.28	1.28	1.28	0.37	0.37	0.37	0.37	0.37	0.37
2	0.56	0.52	0.52	0.84	0.54	0.47	0.50	0.44	1.53	1.42	1.62	1.53	1.40	1.38	nd	nd	nd	nd	nd	nd
5	0.95	0.58	0.89	1.36	0.93	0.69	1.0	0.71	1.92	1.89	2.02	1.92	1,53	1.41	nd	nd	nd	nd	nd	nd
10	1.57	1.30	1.53	2.36	1.46	0.90	1.38	1.05	2.55	2.36	2.81	2.53	1.89	1.66	1.85	1.62	2.0	2.25	1.1	3.49
40	6.70	4.19	5.32	4.07	4.57	2.6	4.31	nd	nd	nd	nd	nd	nd	nd	6.48	5.99	7.73	4.24	2.18	4.36
60	7.15	5.52	7.44	6.07	6.64	3.7	6.30	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
80	9.70	7.19	9.56	8.08	8.60	4.5	7.84	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

nd = not determined

mmhos/cm = millimhos/cm

GENERAL CONCLUSIONS

Physical analysis showed that these soils which were taken from the banks of the Forth estuary, and had been flooded by estuarine water, had a very fine texture. The permeability of the gleyed soil was less than brown earth.

Chemical analysis showed that of the three soil samples studied (muck, gleyed and brown earth soil samples), the gleyed soil had high concentrations of Na, Mg and Cl while the muck soil had intermediate values for these ions. The brown earth had the same amount of Ca as the gleyed soil, but a higher percentage of exchangeable Ca which is supported by analysis of standing water and plants covering the sample sites.

An interest in saline soils lead to this study on the effect of salts on the solubility of certain ions which are generally present in high quantities in saline soils and are also important nutrients.

The effect of adding salts on the solubility of native phosphate in the soil was shown to decrease it. It was clearly shown that the type of salt made very little difference. The actual concentration of salt had more effect in decreasing the solubility of phosphate. This revealed that soil salinity restricts the amount of soluble phosphate in soil solution. This could have the beneficial effect of reducing water pollution.

Phosphate was added to the soil samples and in almost every case the addition of salt reduced the phosphate solubility. This was due to the retention of phosphate by soil and to the formation of insoluble phosphate salts. The effect of salt was found to increase the retention of phosphate. Similar results were shown more clearly when very high concentrations of phosphate were added.

The uptake of cations by soil was shown to vary with the type of salt and concentration. It was shown that the ability of soil to adsorb cations depended on exchange capacity. The top soils had higher concentrations of cations dependent on exchange capacity. The top soils had higher cation adsorption than the sub soil due to the organic matter content.

Soils with high exchange capacity need more $CaSO_4$ or $CaCO_3$ for their reclamation. They also need more fertilizer.

The displacement of different cations from soils shows the importance of considering the interactions which occur in the soil when choosing the composition and level of a particular fertilizer.

In saline soil the addition of either monovalent or divalent cations displaced divalent cations, but in non saline soil little displacement of divalent cation by monovalent cations was noted.

Experiments were carried out in which powdered $CaCO_3$ and $CaSO_4$ were added to soil samples, since some saline soils in Iraq have these salts in high concentrations.

The effect of salts on soils with $CaCO_3$ was to increase the dissociation of Ca and change the pH. Usually the creating of a saline alkaline soil leads to deficiencies of most elements. This highlights the problem which arises on irrigating a calcareous soil. Such a soil has to be reclaimed by leaching, and subsequent treatment with sulphur to lower the pH.

Conductivity measurements were made to find the fraction of salt ionized qualitatively. The addition of monovalent salt was found to increase conductivity more than did divalent, thus indicating that monovalent salts have the more important effect on soil salinity.

The effect of low concentrations of salt, up to 10 meq/l had proportionally more effect than had high concentrations 40 meq/l up to 80 meq/l. This can be explained in terms of the ionic strength and activity coefficients of ions.

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