MATHEMATICAL MODELLING AND SIMULATION OF IONS CONCENTRATION IN SOIL WATER.

(A CASE STUDY OF UPPER NIGER BASIN DEVELOPMENT AUTHORITY, MINNA.)

BY

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CERTIFICATION

This is to certify that the project was supervised moderated and approved by the following under listed persons on behalf of the Chemical Engineering Department, School of Engineering and Engineering Technology, Federal University of Technology, Minna.

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DEDICATION

This research work is dedicated to Almighty Allah for making it possible for successful completion of my first-degree programme. And also to my parents and siblings who are always for my success in life.

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SYMBOLS

(1)	G_r	The free energy change of reaction.	KJ/mol
(2)	G_r^o	Standard free energy change of reaction.	KJ/mol
(3)	K_{eq}	Equilibrium Constant Reaction	
(4)	α	Mole of reactant A.	mgmol/L
(5)	β	Mole of Reactant B	mgmol/L
(6)	φ	Number of mole (cm^{-2})	
(7)	φ^o	Number of mole (cm^{-2}) in solution at time $t = 0$	
(8)	r^+	Progressive rate of reaction	
(9)	θ_H	Fraction of adsorption site occupied by H^+	
(10)	θ_ε	Fraction of adsorption site occupied by H^+	
(11)	Xm	Fraction of surface of M_2Site occupied by M_2 Cation	
(12)	K	Equilibrium constant for adsorption.	
(13)	M_H	Concentration of H^+ in the solution	mg/L
(14)	n_{Hpx}	Moles of Hydrogen.	mgmol/L
(15)	n_{m2px}	Moles of Cations	mgmol/L
(16)	C_c	Concentration of the cations	mg/L

ABSTRACT

The work involves the modelling and simulation of ion concentration in soil water. The ions considered are sodium (Na^+), magnesium (mg^{2+}) potassium (k+). Data were collected from upper Niger River Basin Development Authority (UNRBDA) which is my case study. A theoretical (physical) model was generated which enable one to predict the concentration of these ions in soil water. The simulated value obtained for Na+, P^{3+} mg^{2+}, K^+, N^-, Ca^{2+} were 1.566mg/l, 0.0214mg/l, 3.7919mg/l, 1 .9917mg/l, 14.8363mg/l, 9.5717mg/l as compared to experimental which were 1.50mg/l, 0.03mg/l ,3.88mg/l, 2.00mg/l, 14. 50mg/l and 9.60mg/l respectively. From comparison these values were closed enough it is recommended that the developed model could be used by the authority in planning and managing their irrigation programme

CHAPTER ONE

1.0 INTRODUCTION

1.1 BACKGROUND OF THE STUDY

Salts are added to groundwater passing through soil by soluble products of soil weathering and of erosion by rainfall and flowing water. Excess irrigation water percolating to the water table may contribute substantial quantities of salts. water passing through the root zone of cultivated areas usually contain salt concentrations several time that of the applied irrigation water increases result primarily from the evapotranspiration process, which tends to concentrate salts in drainage. In addition, soluble soil materials, fertilizers, and selective absorption of salts by plant will modify salt concentration of percolating water. Factors governing the increase include soil permeability, drainage facilities, Amount of water applied, crops and climate. Thus high salinities maybe found in soil and ground water of arid climate where reaching by rain water is not effective in diluting the salts solutions similarly, poorly drained areas, particularly bashing having interior drainage often contain high salt concentration.

Some salts are highly soluble, a consequence of which they become depleted in the soil. At the nitrates, acetates and all the common chlorides are soluble (except those of lead, silver and mercurous mercury)

Precipitation reaching the earth contains only small amount of dissolved mineral matter. Once on earth the water reacts with the minerals of the soil and rock in contact with it, the quantity and type of mineral matter dissolve depend on the chemical composition and physical structure of the rocks as well as the hydrogen-ion concentration (pH) of the water.

Carbon dioxide ($C0_2$) in solution, derived from the atmosphere and from organic processes in the soil, assist the solvent action of water as it moves underground. Ordinarily, higher concentrations of dissolved constituents are found in groundwater than in surface water because of the greater exposure to soluble materials in geologic strata. (David Keith Todd 1992) Soluble salts in ground water originate primarily from solution of rock materials. Bicarbonates, usually the primary anion in ground water, is derived from carbon dioxide ($C0_2$) released by organic decomposition in the soil salinity varies with specific surface area of aquifer materials. Solubility of minerals and contact time, value tends to be highest where movement of ground water is least; hence, salinity generally increases with depth.

In the lower part of the soils strata, aid deeper in the ground, the dissolved compounds in water consist mostly of carbonate, sulphate(s), calcium(Ca), magnesium (mg), sodium (Na) and potassium (K) ions with (usually) small amount of chloride (cc), iron (fc) and silica. Common dissolved gases include carbon dioxide ($C0_2$), Nitrogen (N_2), oxygen (O_2), methane (CH_4), and hydrogen sulphide (H_2S) (Adeniyi, 2001).

1.2 AIMS AND OBJECTIVES

The objective of this study is to develop a mathematical model and simulation technique to determine the rate of depletion of ions in the soil by considering the basic principle of soil thermodynamics and reaction kinetics, which is aimed at:

Predicting the concentrating of various cation (Ca^{2+}, mg^{2+}, K^+, NO_3^{2-}, Na^+ and $P0_3^-$) within Niger State.

1.3 SCOPE OF THE STUDY

The scope of work is restricted to the data obtained from various chemical analysis of soil water from some irrigated site within Niger State by the Upper Niger River Basin Development Authority (UNRBDA).

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 WEATHERING PROCESSES

Weathering refers to the disintegration and alteration of rocks and minerals by physical and chemical process. Physical weathering is caused by physical stresses within the rock or minerals. It causes the rock to disintegrate into smaller sized material, without changing the chemical composition. Chemical weathering is caused by chemical reactions and definite chemical changes occur in the weathering products.

In nature, both physical and chemical weathering may occur simultaneously. However, usually precede soil formation from solid rocks. Although, by nature, physical weathering is of more importance at or near the soil surface, occasionally it may take place below the soil surface. Plants roots may contribute to physical weathering below the soil surface by growing into cracks; they rapture the rocks a parts (Kim-H.Tan 1992).

Chemical weathering occur at the soil surface in the solum (the solum (plural sola) of a soil consist of a sets of related horizons) (soil survey staff 1981) or below the solum (in the parent material).

Therefore, Jackson and Sherman (1953) divided it into pedo chemical and geo chemical weathering. Pedochemical weathering refers to chemical weathering within the solum, whereas geochemical weathering is weathering below the solum.

Essentially, a sharp separation between pedo and geo chemical weathering as reported by Boul et al (1973) is difficult to realize in nature.

Regardless of this difference in opinion, weathering in general results in decreases of soluble material, and in the synthesis of new materials. (Clay and humus).

2.1.1 IGNEOUS ROCK

The round water passing through igneous rocks dissolves only very small quantities of mineral matter because of the relative insolubility of the rock composition percolating rainwater contain carbon dioxide ($C0_2$) derived from the atmosphere, which increase the solvent action of water. The silicate mineral of igneous rocks result in silica being added to the ground water.

There is a silicate mineral with a chain structure, the pyroxene groups. The pyroxenes are common in igneous rocks. In fact, some igneous rocks (logically called pyroxenites) are composed almost entirely of pyroxene yet it is often difficult to recognized pyroxenes in rocks and to distinguish them from several other minerals, notably the amphiboles, by purely megascopic method.

Pyroxenes are solid solution of great complexity, all of which have the basic formula $XY[(Si, AL)O_3]_2$ where X maybe Na^{+}, Ca^{2+}, Mn^{2+}, Fe^{2+} and Li^{+} and Y maybe mn^{2+}, fe^{2+} mg^{2+}, fe^{3+}, AL^{3+}, Cr^{3+} & TI^{4+}.

2.1.2 SEDIMENTARY ROCKS

Sedimentary rocks are more soluble than igneous rocks (the important mineral in sedimentary rocks are feldspar, gypsum, and forms of calcium carbonate). Because of their high solubility, combined with their great abundance in the earth crust, they finish a major portion of the soluble constituent to ground water. Sodium (Na) and calcium (Ca) are commonly added cations; bicarbonate and sulphate are corresponding anions chloride occurs to only a limited extent under normal conditions; important sources of chloride however are from sewage and intruded seawater. Occasionally nitrate ($N0_3$) is an important natural constituent; high concentration may indicate sources of part or present pollution. In limestone terrains calcium and bicarbonate, ions are added to the groundwater by solution.

2.2: THE NATURAL SOURCES AND CONCENTRATION OF THE PRINCIPAL CHEMICAL CONSTITUENTS IN GROUNDWATER.

TABLE 2.1 The Principal Chemical Constituents Inground Water And Their Sources, Concentrations And Effect On Usability. Which Is Modified From C.N Dureer & E. Baker, Usgs Water-Supply Paper 1812, 1964.

Constituents	**Major Natural Sources**	**Concentration in Natural Water**	**Effect on Usability of water**
Silica ($SiO2$)	Feldspars, feromagnesium and clay minerals, amorphous silica chert, opal	Ranges generally from 1.0 to 30mg/L, although as much as 100 mg/L is common: as much as 400mg/L found in brines.	In the presence of calcium and magnesium, silica forms a scale in boiler and on steam turbines that retards heat: the scale is difficult to remove. Silica may be added to soft water to inhibit corrosion of iron pipes.
Manganese (Mn)	Manganese in natural water probably comes most often from soils and sediments. Metamorphic and sedimentary rocks and mica biotite and	Generally 0.2mg/L or less groundwater and acid mine water may contain more than 10mg/L	More than 0.2 mg/L precipitates upon oxidation, causes undesirable taste deposits on foods during cooking, stains plumbing fixtures and laundry and foster growth in reservour, filters and distribution systems. Most industrial users

	amphibole hornblende minerals contain large amounts of manganese.		object to water contain, more than 0.2mg/L
Calcium (Ca)	Amphiboles, feldspar, gypsum pyroxenes, aragonite, calcite dolomite, clay minerals.	Generally less than 100mg/L brines may contain as much as 75,00mg/L	Calcium and magnesium combine with bicarbonate, carbonate, sulphate and silica to form heat retarding, pipe dogging scale in boiler and in other heat – exchange equipment. Ca and Mg combines with ions of fatty acid in soaps to form soap suds; the more calcium and magnesium, the more soap required to form suds. A high concentration of magnesium has a laxative effect, especially on new users of the supply.
Magnesium (Mg)	Amphiboles, olivine, pyroxenes, dolomite, magnetite, clay minerals	Generally less than 50mg/L; ocean water contains more than 1000mg/L, and brines many contain as much as 57,000mg/L	
Sodium (Na)	Feldspars (albite): clay minerals; evaporates, such as halite (NaCl) and mirabilite (Na2SO4.10H20);	Generally less than 200mg/L about 10,000mg/L in sea water; about 25,000mg/L in brines	More than 50mg/L sodium and potassium in the presence of suspended matter causes foaming, which accelerates scale formation and corrosion in boilers; sodium and potassium carbonate in recirculating

Potassium (K)	industrial waste Feldspars (orthoclase) and micro cline), feldspathoids, some micas, clay minerals	Generally less than about 10mg/L; as mush as 100mg/L in hot springs; as much as 25,000mg/L in brines	cooling water can cause deterioration of wood in cooling towers. More than 65mg/L of sodium can cause problems in the manufacture.
Nitrate (NO3)	Atmosphere; legumes, plant debris, animal excrement.	Commonly less than 10mg/L	Water containing large amount or NO3 (more than 100mg/L) is bitter tasting and may cause physiological distress. H2O from shallow well containing more than 45mg/L has been reported to cause methemoglobinemia in infants.

2.3 SOIL COMPOSITION

The soil system is composed of 3 phases; solid, liquids and gas. The solid phase is a mixture of mineral and organic material and provides the skeletal framework of the soil. Enclosed within this framework is a system of pores, shared jointly by the liquid and gaseous phase.

The spatial arrangement of the solid particles and associated pores or void is, in micropedological terms, the soil fabric (Kubiena, 1938; Brewer and Sleeman, 1960). The nature of the soil constituents, the activity of soil organisms, and other soil-forming processes leads to the creation of a series of features with specific soil fabrics. Although the traditional concept indicates that soil fabrics is comparable with rock fabric, which depends on the shape and arrangement of minerals, it is perhaps more appropriate to compare soil fabric with the fabric of plant and animal tissue. The components of the soil fabric include water and organic substances, containing humus and organisms, and a series of organic and inorganic compounds. These materials are also of importance in plant and animal tissue; rocks do not contain these compounds.

There are four principle ways in which ions in the soil gives the product of dissociation of salts in the soil water solution.

1. By interaction of two salts.

   Example: $2NaHC0_3 + MgSO_4 \longrightarrow Mg(HCO_3)_2 + Na_2 SO_4$. ------------(2.1)

2. By interaction of an acid and base e.g.

   $HCL + NaOH \longrightarrow Nacl + H_2O$ ----------------------------------(2.2)

By direct combination of a metal and a non-metal

Example $Na + CL \longrightarrow Nacl$. --(2.3)

By a metal more active than hydrogen that displaces hydrogen from an acid, e.g. $Na^+ + H_2CO_3 \longrightarrow NaHCO_3 + H$ ------------------------(2.4)

Among the common metals that are more active than hydrogen, that can displace it are potassium (K most active), barium (Ba), Calcium (Ca), Sodium (Na) Magnesium (mg), aluminum (Al), manganese (Mn) and iron (Fe) least active of these)

Moreover, the more actives ones as well as hydrogen (i.e. Ca can displace Na).

Most salts are metals, but some contain displaceable hydrogen e.g. $NaHCO_3$ and in a sense these are acid salts. (Adeniyi, 2001).

2.3.1 pH

pH:- pH is the reciprocal of the logarithms of the concentration of hydrogen ion in water, which is expressed in gram-ion per litter.
(Belan 1981)

$$\text{Log}\frac{1}{H+} = pH \text{---------------} (2.5)$$

In acid medium H+ must be less than 10-7 and in alkaline medium H+ must be greater than 10-7

The expression pOH = log 1/OH --------------------(2.6) is referred to as the hydroxyl value. It follows that after the logarithm is found, equality can be reduced tot he form.

$Pkw = P^{OH} + pH = 14$ (t = 298k) ------------------ (2.7)

The relationship between pH and other water quality parameters such as alkalinity, carbon dioxide and ionic strength, governs the solubility of calcium carbonate which is commonly used to provide a protective scale on interior pipe surface. To deposit this protective scale, the pH of the water must be slightly above the pH of saturation for $CaCO_3$, provided sufficient calcium are present (Pontius et al 1943). pH adjustment alone is often insufficient to control corrosion in water that are low in carbonate or bicarbonate alkalinity. A protective coating of caco3, for instance will not form unless a sufficient number of carbonates and calcium ions are present in the water (Pontius et al 1943).

The proper pH for any given water-distribution system is so specific to its water quality and system materials that only general guidance can be provided. If the water contains a moderate amount of carbonate alkalinity and hardness, the pH of such water would also be moderate.

The adjustment of pH is the most common method of reducing corrosion control for several reasons.

1. Hydrogen iron (H^+) act as electron acceptor and enter readily into electrochemical reactions. Acid water are generally corrosive because of the high concentration of hydrogen ions.
2. pH is the major factor that determines the solubility of most pope materials. Most materials used in water distribution systems (copper, zinc, iron, lead and cement) dissolve more readily at a lower pH. Increasing the pH, increases the hydroxide ion (OH^-) concentration, which in turn decreases the solubility of metals that have relatively insoluble hydroxides, basic carbonate and oxides, including copper, zinc, iron and lead? When carbonate alkalinity is present, increasing the pH, up to a point increases the amount of carbonate ion in solution. This may control the solubility of metals that have insoluble basic carbonates, such as lead, and copper (George etal, 1979).

2.4 ADSORPTION

2.4.1 TYPES OF ADSORPTION

The process of concentrating materials at the interface is called adsorption. It is one of the reactions attributed to the surface chemistry of soil colloids. Materials that decrease surface energy will be concentrated at the liquid – vapour interface, whereas materials that decrease interfacial energy will concentrate more n the liquid-solid interface (Gortner and Gortner, 1949). Adsorption in soils is more the type of concentrating material at solid-liquid interfaces. This type of adsorption can be distinguished into positive and negative adsorption. Positive adsorption is the concentration of the solute on the colloidal surface. It is also referred to as specific adsorption, the solute usually decrease surface tension. On the other hand, negative adsorption is the concentration of the solvent on the clay surface, the solute is then concentrated in the bulk solution; here surface tension is increased.

2.4.2 ADSORPTION ISOTHERMS

Adsorption was defined earlier on the concentration of constituents at the colloidal surfaces. The curve of relating the concentration of absorbed materials at a fixed temperature is called the adsorption Isotherm.

There is no general agreement in the literature on the nature of adsorption isotherms. (Bailey and White 1970) are of the opinion that adsorption's of organic matter can be better described with the freundlich equation, but (1970) has reported that adsorption organic matter follows the langmuir equation. According to the freundlich equation theoretically, adsorption increases indefinitely with increasing concentration. On the other hand, the langmuir equation indicates that adsorption of organic matter on the clay surface tends to reach maximum limit. The latter is compatible with the fact that soil and clay do not have an infinite capacity to absorb, but will sooner or later be saturated.

2.5 CATION EXCHANGE

2.5.1 ADSORPTION OF CATION BY SOIL COLLOIDS

Since clay colloids carry negative charges, cations are attracted to the clay particles. This is Mother Nature's condition to maintain electro neutrality in soils. These cations are held electrostatiscally on the surface of the clay. Most of them are free to distribute themselves through the liquid phase by diffusion the density of ion population is greatest at or near the surface. These cations are called Adsorbed cations. Different rates and orders of adsorption are drawn among the cations, since the adsorption reaction depends on the surface potential, valence, and hydrodynamic radius. As surface potential increases, more of the divalent ions will be adsorbed. Trivalent cation would even be more strongly concentrated on the clay surface exhibiting high surface potential values. When a mixture of monovalent and divalent ions is present in a soil solution, adsorption is usually shifted in favour of the divalent ions. The hydrodynamic radius also affects specific adsorption of cations. The crystalline radius, on the other hand, plays only a minor role. Generally, ions with smaller hydrated sizes are preferably absorbed, the following decreasing order of preference for adsorption of monovalent cations by clays has been reported (Gast, 1977).

Cs > Rb > K > Na > Li

The rate of adsorption for Cs, is the highest, because Cs is the smallest in hydrated size. The ion has a thin hydration shell, which makes a close approach to the clay surface possible. Lithium, on the other hand, has the largest hydrodynamic radius. Its thick hydration shell increases the distance from the ion to the clay surface. Such a series of ions, listed in decreasing order of preferential adsorption, is called a lyotropic series for divalent cations has also been reported in the literature (Taylor and Ash Croft. 1972).

Th > La > Ba > Sr > Ca > Mg.

Evidence is present that different lyotropic series exist for different types of clays.

2.5.2 CATION EXCHANGE REACTIONS

The term cation exchange is preferred over the term base exchange, since the reaction also involves H+ ions. The hydrogen ion is a cation but not a base. The adsorbed cations can be exchange by other cations, hence the cation are also exchangeable cations. The rate of reaction is virtually instantaneous. To maintain electro neutrality in the soil, exchange reaction are stroichiometric reactions an illustrated by the classic experiment of way (1850)

$Ca - soil + 2NH_4^+$ ------- $(NH_4)_2 - soil + Ca^{2+}$ ------------------------(2.8)

Adsorption and cation exchange are of great practical significance in nutrient uptake by plants, soil fertility, nutrient retention and fertilizer application. Adsorbed cation is generally available to plant by exchange with $H+$ ions generated by the respiration of plant roots. Nutrient added to the soil, in the form of fertilizers, will be related by the colloidal surfaces and are temporarily presented from leaching cations that may pollute the ground water maybe filtered by the adsorptive action of the soil colloids.

2. 5. 3 CATION EXCHANGE CAPACITY (CEC)

Cation exchange capacity (CEC) of soil is defined as the capacity of soils to absorb and exchange cation scientifically; it is related to the surface area and surface change of the clay.

However, CEC is commonly determined by extraction of the cations from soils with a solution containing a known cation for exchange. The result expressed in milli equivalent per 100g of soils. It is common practice in the determination of CEC to analyze all exchangeable cations. The CEC is then CEC = ∑ meg exchangeable cation per 100g soil.

But According to Bolt etal (1976) is

CEC [∑exchangeable cation –∑exchangeable Anions] in meq/100g. -----(2.9)

2.5.4 ANION EXCHANGE

2.5.5 ADSORPTION OF ANIONS BY SOIL COILDS.

Two types of adsorption by soil colloid are recognised: Negative adsorption and Positive adsorption.

Negative Adsorption of anions occurs at a colloidal surface possessing a negative change. Because of the Latter, cation are attracted and concentrated at the colloid surface. On the other hand, anions are expelled from the double layer formed on the positively changed surface. This exclusions of anion is called negative adsorption therefore the bull solution contains more anions that the solution in the interface. The amount excluded is reported to be a small part of the CEC. Bolt (1976) shows that under conditions prevailing in soil, the negative adsorption of anions is approximately 1- 5% of the CEC.

Positive Adsorption of anions is the adsorption and concentration of anions on the positively charged surfaces or edges soil colloids. Here, negative adsorption of cations (i.e. repulsion of cations by the positive charge) occurs. The anion Exchange capacity (AEC) of soil is usually smaller than the CEC. It is dependent on charges in electrolyte level and as soil pH. It is also limited to special types of clays. (Kim H. Tan 1992).

As with cation, lyotropic series of anions are also available. Bolt (1976) reported a decreasing order of preferential adsorption among the following anions.

$SiO_4 > Po_4 >> So_4 > NO_3 > Cl^-$

This lyotropic series indicates that SiO_4 & PO_4 in the strongly adsorbed; SO_4 and NO_3 ions are absorbed in considerably lower concentration or are often not adsorbed. At a neutral soil reaction, or pH > 6. Positive adsorption of SO_4 and Cl^- is very small. These two anions are generally subject to negative adsorption, in contrast with phosphate ions that are adsorbed more by positive charged surfaces or edges or clay minerals.

$Al - OH + H_2PO_4 \rightleftarrows L\text{-}H_2PO_4 + OH-$ ----------------------------------(2.10)

The reaction is prevalent in acids soils. It results in a strong bond between the phosphate ion and the octahedral AL. Frequently only part of the phosphate can be recovered by, desorption analysis.

2.6 FERTILIZERS

Fertilizing consists of 3 basic element and this element are very important to plant growth and are widely applied to soil as inorganic fertilizers. These elements are Nitrogen (N), Phosphorous (P) and Potassium (K).

Since the early reviews of Allison (1955 & 1966) in which levels or "Unaccounted – for – N" in Nitrogen fertilizer budget were as high as 50% it contain up to 80% in the used of Ammonia (NH_3) and Nitrogen liquids. These materials are expensive and suffer from problem of gaseous loss to the atmosphere. The tend to be used for large-scale fertilizing operations only and must be placed at depth in the soil to maintain efficiency.

In addition, below is the Nitrogen Cycle, relevant to Nitrogen Fertilizer budgeting.

TABLE 2.2: The Nitrogen Cycle Relevant to Nitrogen Fertilizer Budgeting

Types of Process	**Process description**
Storage	Chemical fixation of NH_4 by cation exchange on positively charges soils colloids.
Transformation	1. Ammonification Mineralization of organic Nitrogen manures by a wide range of decomposer organism. 2. Nitrification Bacteria transformation of NH_4-N firstly to NO_2-N by Nitrosomanas then to NO_3-N by nitrobacter. 3. Denitrification reduction of NO_3 to NO_2 followed by reduction to the gases N_2O,NO,NO_2
Transport	1 NO_3 leaching, Nitrate is particularly soluble and subject to mass flow and drainage out of soil profiles during storm events. 2 Volatilization (gaseous loss to the atmosphere) a. N_2O, NO, N_2 after denitrification has b. NH_3 gaseous losses from NH_4 fertilizer applied to calcareous soil and through urea hydrolysis.

The dynamic of fertilizer phosphorus in soil thus depend on differential dissolution, adsorption and precipitation process, with the production of various fertilizer reaction products. Three major controls on the fate of applied phosphorous fertilizer are thus:

a. The form in which phosphorous is applied

b. The phosphorous adsorption capacity

c. Soil condition such as pH and Eh, which control solubility and precipitation reactions.

The solubility of phosphorous fertilizer applied to soil depends on their mineral form, grain or granule size and on soil condition, particularly moisture content and pH. Rock phosphate has been clarified by McClellan and Gremillion (1980) into (a) Ca-phosphate (capatities) (b) Ca-Fe-Ac phosphate and (c) Fe and Al phosphate such as strengite ($FePO_4.2H_2O$) and variseite ($ALPO_4.2H_2O$).

By far the most important of these commercially are the apatite at pH above 6-6.5, rock phosphate are practically insoluble or, at best, sparingly soluble to improve solubility for agricultural soil, rock phosphate are treated with sulphuric acid to produce super phosphate and triple super phosphate fertilizer respectively.

Most Agricultural soil show fairly high crop uptake efficiency for potassium fertilizer (fink, 1982) and only rarely, on light soils, are high leaching losses associated with potassium fertilization Cooke (1966) suggested that one of the main inefficiency in K fertilizing is due to "luxury consumption" when crops take up more potassium than they need to give a maximum yield. These observations suggest that exchange and fixation of potassium on soil colloids act not only to retain potassium in the rooting zone, where plant roots can use it efficiency, but also to prevent potassium leaching losses in drainage waters. This efficient retention can lead to the build up, particularly in clay soils of substantial residual potassium fertilizer.

Below are the compositions of some commonly used fertilizers. Data tabulated from Cooke (1980).

TABLE 2.3 Composition of Some Commonly Used Fertilizer

a. Nitrogen	Percentage Nitrogen Composition
Solid:	
Ammonium sulphate $(NH_4)SO_4$	21
Potassium nitrate (KNO_3)	13.8
Ammonium chloride (NH_4Cl)	26
Ammonium nitrate $(NH_4)NO_3$	35
(nitro chalk, if mixed with $CaCO_3$	
Urea (carbanide) $CO(NH_2)_2$	46
Calcium cyanamide $CaCN_2$	21-22
Liquids:	
Ammonia gas liquors (dilute NH_4 solution)	1-4
Aqueous Ammonia gas (NH_3)	21-29
Anhydrous Ammonia gas (NH_3)	82
b. **PHOSPHOROUS**:	**% P composition**
Single super phosphate $Ca(H_2PO_4)$: $CaSO_4$	8-9.5
Triple super phosphate $Ca(H_2PO_4)_2$	20
Mono ammonium phosphate $(NH4)H_2PO_4$	20-30
Di ammonium phosphate $(NH_4)_2HPO_4$	21
Ground mineral phosphate GMP And Crushed Rock phosphate (CRP)	12.5
c. **POTASSIUM:**	**% K Composition**
Muriate of potash (potassium chloride)KCL	50
Sulphate of potash (potassium sulphide) K_2SO_4	40-42
Salt Detre (potassium nitrate) Kno_3	36

2.7 CHEMICAL THERMODYNAMICS OF SOIL REACTIONS.

Chemical thermodynamics is the science of energy relations within chemical systems. In any chemical reaction, energy changes are occurring. A system that is not in equilibrium will spontaneously under go changes by releasing energy. At equilibrium, the energy changes of the reactant must equal the energy changes of the products, and the following relationship is valid.

$\Delta Gr = \sum$ free energy products $- \sum$ free energy reactant $= 0$.

The equation expresses the first law in thermodynamics,

For a general reaction $A + B \rightleftarrows C + D$, the free energy change of reaction in thermodynamics is written as:

$$\Delta Gr = \Delta G^\circ r + RT \ln \frac{(C)(D)}{(A)(B)} \text{ ------------------------------- } (2.11)$$

or

$$\Delta Gr = \Delta G^\circ r + RT \ln K. \text{ -- } (2.12)$$

Where

ΔGr = Is the free energy change of reaction.

$\Delta G^\circ r$ = Standard free energy change of reaction.

K= The Activity ratio.

If ΔGr, has a negative value, the reaction will go spontaneously to the right, but ΔGr is positive the reaction will occur in the reverse direction.

If on the other hand $\Delta Gr = 0$, then in accordance with first law of thermodynamics, the reaction is at equilibrium. At equilibrium the activity ratio equals to equilibrium constant K_{eq}. K_{eq} is also known as the thermodynamics equilibrium constant. Consequently, at equilibrium condition the following relation is valid,

$$\Delta Gr = 0\ \Delta G^\circ r + RT \ln K_{eq} \text{ --- } (213)$$

Therefore

$$\Delta G^\circ r = - RT \ln K_{eq} \text{ -- } (2.13)$$

$$\Delta G^\circ r = - 1.364 \log K_{eq} \text{ --- } (2.14)$$

25°C = 298K

2.8 EQUILIBRIUM CONSTANT AND ION PAIRS

Ion pairs are defined as pairs of oppositely charged ions that behave as a thermodynamics entity (Davies, 1962). Strong electrolytes often will not dissociate completely into their components ions. Because of short-range interactions between closely adjacent cations and anions, these ions remain strongly attracted to each other. Therefore, a considerable portion may behave as if they were not ionized at all.

Pairing of ions can be illustrated as follows with Ca and Co_3

$CaCo_3 \rightleftarrows. Ca + Co_3$ ---(2.15)

In which CaCo3 is the Ca^{++} - $CO3^{--}$ pair. The equilibrium constant of such a reaction is

$$Keq = \frac{(Ca)\,(Co_3)}{(CaCO_3)}$$ ---(2.16)

Although Keq is formulated in away similar to that of weak electrolytes, the dissociation of ions pairs is affected by forces different from those in weak electrolyte.

Soil cations and anions that have been reported to pair extensively are H+, K^+, Na^+, OH^-, HCO_3 and SO_4, Cl^-, ions do not form ions pairs with other cation to any measurable amounts (Garrels and Chist 1965, Davies 1962).

2.9 THE KINETIC ORDER OF CHEMICAL REACTIONS

The equation.

$\alpha A + \beta B \longrightarrow \gamma C$ --(2.17)

Describe the reaction of αmol. Of A with βmol of B to produce γmol of product C. the reaction is illustrated in the figure the rate of change in concentration of reactants A and B with time is give by:- $\frac{d[A]}{dt}$ and $-\frac{d[B]}{dt}$ respectively

(Where square brackets represent concentration). [Sheik Ross 1953]

These values are negative since both A and B diminishes through time.

The rate of change in concentration of product C is given by $\frac{d[C]}{dt}$ since it Accumulated through time. For equation 1, mol. of A are used for every B mo. of B in the production of mol. of C. Thus, the rate of change of [A], [B] and [C]are

$$\frac{-1\, d(A)}{\alpha\, dt} = \frac{-1\, d(B)}{\beta\, dt} = \frac{+1\, d(C)}{\gamma\, dt} \text{-------------------------}(2.18)$$

The mathematics expression-relating rate of reaching to concentration n is called the differential rate law. In equation 1, if $\alpha = 2$, $\beta = 03$ and $\gamma = 1$
Then the differential rate law takes the form.

$$\frac{-1}{2}\frac{d(A)}{dt} = \frac{-1}{3}\frac{d(B)}{dt} = \frac{d(C)}{dt} = K\,(A)^{n}\,(B)^{m} \text{---------}(2.19)$$

Where the experiment n and m are integers or half integers; ii called the order of reaction with respect to A and M is the order of the reaction with respect to B. The sum m + n is called the overall order of the reaction.

The alteration of mineral surfaces during weathering, through ion substitution, exchange and teaching, is thought to change the rate of surface reaction these reaction have been widely studied for feldspar mineral (wollast, 1967; Busenberg and clemency 1976 site example) and for magnesium silicates (luce, Barlett and paole 1972). In an empirical study of the dissolution of serpentine, fosterite and enstatile, luce et al (1972) found that there was an initial rapid exchange of surface mg^{2+}ions for H+ ions, followed by a longer period of hydrogen exchange and extraction of internal magnesium and silicon.. In the experiment, finely ground mineral was leached with solutions whose PH was adjusted in the range 3.2 – 9.6 using HNO_3 or KOH and rate of release of mg and SiO_2 were measured over time periods ranging from 16 to 100h. After an initial period of rapid surface exchange, amount of dissolved mg and Sio2 were proportional to the square root of prime such that;

Where Q = number of moles Cm^{-2} in solution at time t.

K = First order Parabolic rate constant

Q^0 = number of moles Cm^{-2} in solution at time $t = 0$

CHAPTER THREE

3.1 MATHEMATICAL MODELLING AND SIMULATION

Mathematical models of a system only represent the mathematical aspects of a process or system of interest it gives the description of the process, both the physical and chemical phenomena taking place therein. A model retains the physical properties of the system, it is therefore aimed at providing the simplest possible description of a system which is an exact scale down replica of the prototype and at the same time retain its physical character (William, 1995). Process simulation is the representation of a process by mathematical model, generally in form of a computer program. The model can be solved to obtain information about the performance of the process. Process simulation programs are useful tool in design and process synthesis. A computer simulation can be used to predict the effect or changing conditions and capacity on mass and energy balance and to optimising operation easily and quickly (William, 1995).

In the process of model building, system analysis must initially be undertaken. A lot of decision must be made which are crucial for further development these includes finding solution of following (James et al., 1981).

1 Model aims must be stated clearly and unambiguously as possible.

2 Various kinds of constraints and omissions must be taken into account.

3 General assumptions and omissions must be carefully argues.

4 The possibilities of measurement and experimentation on the system being studies must be investigated.

5 A solution strategy must be chosen. This may include methods of collection and analysis of data, estimation of parameters, type of model, available computational facilities and flexibility of simulation tools, generality of solution, possibilities of model extension etc.

Modelling and simulation are inseparable procedures. They include

Modelling and simulation are inseparable procedures. They include complex activities associated with the construction of model representing real processes and experimentation with the model to obtain data on the behaviour of the system being modelled. Modelling deals primarily with the relationships between actual dynamics of the process, model simulation refers to the relationship between the model and simulation, while the model time response is a reflection of the stipulations effect on the process output, in other words, its sensitivity. In recent time, the modelling and simulation approach has become increasingly unavoidable for solving difficult kinds of practical problems.

Mathematical model of dynamic systems and computer simulation find application in technical areas. The purposes of studying systems though the modelling and simulation approach is to achieve different goals without actually constructing or operating real processes. These goals of modelling and simulation may include the following (James, et al., 1981).

1. To improve understanding of some mechanism in the studied process.
2. To predict the system behaviour in different situation where any level of predictive ability represents a benefit.
3. To enable the design and evaluation of synthesised control system.
4. To estimate the process variable which are not directly measurable.
5. To test the sensitivity of system parameters
6. To optimise system behaviour and efficient fault diagnose.
7. To verify models obtained in some other ways

Though, a variety of modelling technique and simulation tool exists, neither the computer nor the tool can completely replaced human decision, judgement and experience which still plays a significant role in determining the validity and usefulness of models for practical application (James et al., 1981).

Since modelling serves as a tool for predicting its therefore useful in this project. The depletion of cations in soil because of many activities can lead to a case in which a given soil is totally depleted of the necessary ions. The development model gives a predictive estimate of nine important cations as a function of the soil pH.

3.2 ASSUMPTIONS.

The following assumptions were made in developing the mathematical equation for the rate reaction in the soil.

1. A clay coil is considered in the equation, because it has the capacity to absorb large quantity of water and therefore more prone to substitution/.exchange reaction.
2. Rate of reaction depends on the pH.
3. The reaction in the soil takes place at standard temperature (25°C)

3.3 EXCHANGE REACTIONS

Chemisorptions is accompanied by a substitution of Ca^{2+}, Na^{+}, K^{+} cations whose attraction with respect to the Oxygen of the crystalline structure in weaker because of their larger diameter (Touray, 1980, Schheidegger andf Sparks, 1996; Perry, 1997). Following lagasa (1981) and talking as an example the weathering of pyroxene, Schott and Berner (1985) proposed (chemisorption's and substitution) the following expression for this surface reaction.

$$M_1M_2Si_2O_6 + 2H^{+} \longleftrightarrow M_2 + M_1H_2Si_2O_6$$

The progressive rate of the reaction can be set as

$$r+ = \frac{dnM_2}{dt} = K^{+} Xm_2\theta_H{}^{2} \tag{3.1}$$

With OH expressed in langmuir Isotherm:

$$K = \frac{\theta_H}{M_H - \theta_H)} \tag{3.2}$$

$$Xm_2 = 1 - X_H \tag{3.3}$$

Where: θ_H = fraction of the adsorption site occupied by H^{+}

θ_E = fraction of the adsorption site that is vacant

Xm_2 = fraction of surface of M_2 sites occupied by M_2 cation.

K = equilibrium constant for adsorption.

M_H = concentration of H^{+} in the solution.

Xm_2 and X_H camn be expressed as a function of the moles of M2 cations (nm_2px) and of hydrogen (n_{Hpx}) contained in the M_2 sites of the surface of the pyroxene that is:

$$npx = nm_2px + n_{Hpx} \text{ --3.4}$$

Assuming that the number of moles of pyroxenes protonated at the surface is given by:

$$n_{Hpx} = nm_2x - nm_1x \text{ --3.5}$$

Where nm_2 and nm_1 are the number of moles of cations released in solution from sites M_1 and M_2 Schott and Berner (1985) reached the following expression:

$$r+ = K_1K^2\theta e^2M_H{}^2 - K_1K^2\theta e^2M_H{}^2 \frac{(nm_2s - nm_1s)}{npx} \text{ ------------------------3.6}$$

For a constant pH, equation 3.6 implies a linear relationship between the rate of reaction and moles of pyroxenes protonated at the surface. From equation 3.6.

$$r+ = K_1\left\{K^2\theta e^2M_H{}^2 - K^2\theta e^2M_H\ (nm_2s - nm_1s)\right\} \text{ ------------------------3.7}$$

from the equation 3.1 and equation 3.7 the following expression was reached by (Adeniyi 2001).

$$MH = K\theta\varepsilon\sqrt{\frac{1 - \frac{n_Hpx}{npx}}{Xm\ ½\theta H}} \text{ ----------------------------3.8.}$$

Which gives the reflection of the concentration of any ion in soil relatives to H^+ and it gives the extent of soil saturation. Where the extent is proportional to the inverse of the hydrogen ion concentration. $M_H = 1/m_H$

3.4 MODELLING OF CATION CONCENTRATION (GEOPHYSICAL MODEL)

From the model (Adeniyi 2001) equation 3.8

$$MH = K\theta\varepsilon\sqrt{\frac{\left(1 - \frac{n_Hpx}{npx}\right)}{Xm\ ½\theta H}}$$

From equation 3.4

$$npx = nm_2px + n_Hpx$$

Since nm_2px is the mole of cation of m_2 sites .

Therefore,

$$M_HXm\,½\theta_H = K\theta\varepsilon\sqrt{\left(1 - \frac{n_Hpx}{npx}\right)} \quad \text{---------------------3.10}$$

$$\frac{M_HXm\,½\theta_H}{K\theta_\varepsilon} = \sqrt{\left(1 - \frac{n_Hpx}{npx}\right)} \quad \text{----------------------3.120}$$

$$\left(\frac{M_H\theta_H}{K\theta_\varepsilon}\right)^2 Xm = 1 - \frac{n_Hpx}{npx} \quad \text{------------------3.13}$$

$$\frac{n_Hpx}{npx} = 1 - \left(\frac{M_H\theta_{\varepsilon H}}{K\theta_\varepsilon}\right)^2 Xm \quad \text{---------------------3.14}$$

$$\frac{n_Hpx}{npx} = \frac{K^2\theta_\varepsilon^2 - M_H^2\theta_H^{\ 2}Xm}{K^2\theta_\varepsilon^2} \quad \text{-----------------3.15}$$

$$\frac{npx}{n_Hpx} = \frac{K^2\theta_\varepsilon^2}{K^2\theta_\varepsilon^2 - M_H^2\theta_H^{\ 2}Xm} \quad \text{-----------------3.16}$$

$$npx = \frac{n_Hpx\,K^2\theta_\varepsilon^2}{K^2\theta_\varepsilon^2 - M_H^2\theta_H^{\ 2}Xm} \quad \text{-------------------3.17}$$

$$nm_2px + n_Hpx = \frac{n_Hpx\,K^2\theta_\varepsilon^2}{K^2\theta_\varepsilon^2 - M_H^2\theta_H^{\ 2}Xm} \quad \text{-------------------3.18}$$

$$nm_2px = \frac{n_Hpx\,K^2\theta_\varepsilon^2}{K^2\theta_\varepsilon^2 - M_H^2\theta_H^{\ 2}Xm} \quad \text{---------------------------3.19}$$

$$= \frac{n_Hpx\,K^2\theta_\varepsilon^2 - n_Hpx\,K^2\theta_\varepsilon^2 - M_H^2\theta_H^{\ 2}Xm}{K^2\theta_\varepsilon^2 - M_H^2\theta_H^{\ 2}Xm} \quad \text{-----3.20}$$

$$= \frac{n_H\cancel{px\,K^2\theta_\varepsilon^2 - n_Hpx\,K^2\theta_\varepsilon^2 -}\,M_H^2\theta_H^{\ 2}Xm}{K^2\theta_\varepsilon^2 - M_H^2\theta_\varepsilon^{\ 2}Xm} \quad \text{-----3.21}$$

$$nm_2px \; \frac{n_Hpx\,Xm\,\theta_H^{\ 2}}{K^2\theta_\varepsilon^2 - M_H^2\theta_H^{\ 2}Xm} \quad \text{-------------------------3.22}$$

The expression above is the model equation of moles of ions (cation and anions) and the concentration ($C_c$mg/L) of any cations is determined by multiplying the moles of ions to its molecular weight. the model of equation is now shown below:

$$C_c = \left(\frac{n_H px\ Xm\ \theta_H{}^2 M_H{}^2}{K^2\theta_\varepsilon{}^2 - M_H{}^2\theta_H{}^2 Xm} \right) \text{ x Mol. wt ---------------------3.23}$$

The equilibrium constant K can be evaluated from the equation

$$\Delta G_r{}^o = -RTInK\text{---------------------------------3.24}$$

$$\Delta G_r{}^o = -2.3026RtlogK\text{------------------------3.25}$$

Using $R = 8.314 \times 10^{-3}$ KJ/mol, at $T = 25^oC = 298^oK$

$$\Delta G_r{}^o = -2.30260 \text{ x } 8.314 \text{ x} 10^{-3} \text{ x } 298 \text{ x } logK$$

$$\Rightarrow \Delta G_r{}^o = -5.705logK$$

$$logK = \frac{G_r{}^o}{5.705} \quad \text{--------------------------3.23}$$

Using Albite ($NaAlSi_3O_8$) (clay soil type). The values of $G_r{}^o$ and $G_r{}^o$ of Albite are given below(Ross 1989)

$\Delta G_r{}^o$ (KJ/mol) = - 3708.32 and $\Delta G_r{}^o$ (KJ/mol) = - 43.555

$$\text{Therefore logK } \frac{\Delta G_r{}^o}{5.705} = \frac{-43.555}{5.705} = -7.635$$

$$K = 2.3 \text{ x } 10^{-8}$$

CHAPTER FOUR

4.1 RESULTS AND DISCUSSION OF RESULTS

4.1.1 EXPERIMENTAL RESULTS

The experimental result for the concentrations of some cations(P^{3+}, N^{+}·$K^{+}a^{+}$, Ca2+, Mg^{2+}) from different sites for the year 1995 and 2001 obtained from the quality control laboratory, of the upper Niger river Basin development Authority (UNRBDA), Minna Niger State are presented in table 4.1-4.2

TABLE 4.1 Experimental Soil Water Analytical Result(1995).

SITES	1	2	3	4	5	6	7
SOURCE	RIVER KADUNA AT GUSORO AWOLY	TUNGAN KANO DAM	RIVER GURARA IZOM	RIVER TAFA NEW WUSE	SWASHI DIVERSION DAM	RIVER GALMA AT IGABI	RIVER GALMA AT ZARIA
P^{H}	7.10	7.30	7.30	7.20	7.30	7.10	7.20
Po_4^{3-}mg/L	0.30	0.02	0.00	0.00	0.01	0.00	0.00
NO_3^-mg/L	14.50	0.90	3.00	14.50	6.00	10.00	7.00
K^+mg/L	2.00	2.50	2.00	2.50	1.00	1.00	2.50
Na^+mg/L	1.50	2.50	1.50	1.00	0.50	3.00	0.50
Ca^{2+}mg/L	9.60	16.00	8.00	9.60	16.00	17.60	17.60
Mg^{2+}mg/	3.88	6.80	5.82	5.82	4.85	6.80	5.82
Fe^{2+}mg/L	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn^{2+}mg/	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zn^{2+}mg/L	0.00	0.00	0.00	0.00	0.00	0.00	0.00

TABLE 4.2. Experimental Soil Water Analytical Result 2001

SITE	1	2	3	4	5	6	7
SOURCE	RIVER KADUNA AT GUSORO AWOLU	TUNGAN KAWO DAM	RIVER GURARA IZOM	RIVER TAPA NEW WUSE	SWASHI DIVERSION DAM	RIVER GALMA AT IGABI	RIVER GALM AT ZARIA
PH	7.30	7.40	7.40	7.00	7.50	6.70	7.00
Po$_4^{3-}$ mg/L	–	–	–	–	–	–	–
No$_3^-$mg/L	24.00	22.00	9.01	15.65	27.50	6.75	12.66
K$^+$mg/L	0.260	0.320	0.410	0.370	0.190	0.420	0.460
Na$^+$mg/L	2.99×10^{-3}	0.210	0.095	0.060	0.090	0.610	0.190
Ca^{2+}mg/L	40.00	36.00	20.00	16.00	28.00	16.00	38.00
Mg^{2+}mg/	10.80	9.60	10.80	6.00	15.60	3.60	8.40
Fe^{2+}mg/L	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn^{2+}mg/	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zn^{2+}mg/L	0.00	0.00	0.00	0.00	0.00	0.00	0.00

4.12 Simulated RESULTS [RIVER KADUNA AT GUSORO AWOLU (1995) and this is shown in table 4.3-Table 4.8

TABLE 4.3 Simulated concentration for phosphorous P^{3+} (1995)

n_H (mgmol/L)	Xm=0.05	Xm=0.1	Xm=0.15	
	θ_H=0.06	θ_H=0.1	θ_H=0.14	EXPERIMENTAL
	Cc(mg/L)	Cc(mg/L)	Cc(mg/L)	Cc(mg/L)
0.0000000794	1.59944E^{-}8	9.03115E^{-}8	2.74588E^{-}09	0.03
0.1000000794	0.02144092	0.113742473	0.345829227	
0.2000000794	0.040288167	0.227484855	0.69165818	
0.3000000794	0.060432243	0.341227238	1..037487133	
0.4000000794	0.080576318	0.45496962	1.383316086	
0.5000000794	0.100720394	0.568712003	1.729145039	
0.6000000794	0.120864469	0.682454385	2.074973991	
0.7000000794	0.141008545	0.796196767	2.420802944	
0.8000000794	0.161152621	O.90993915	2.766631897	
0.9000000794	0.181296696	1.023681532	3.11246085	

TABLE 4.4 Simulated concentration for Nitrogen N^+

n_H(mgmol/L)	Xm=0.25	Xm=0.30	Xm=0.35	EXPERIMENTAL
	θ_H=0.22	θ_H=0.26	θ_H=0.3	
	Ccmg/L	Ccmg/L	Ccmg/L	Ccmg/L
0.0000000794	8.6148×10^{-7}	1.68285×10^{-6}	3.3570×10^{-6}	14.50
0.1000000794	1.08439	2.1195	4.2280	
0.2000000794	2.1699	4.2389	8.4560	
0.3000000794	3.2549	6.3584	12.6840	
0.4000000794	4.3399	8.4779	16.9120	
0.5000000794	5.4249	10.5973	21.1400	
0.6000000794	6.5099	12.7168	25.3680	
0.7000000794	7.5949	14.8363	29.5960	
0.8000000794	8.6799	16.9557	33.8240	
0.9000000794	9.7649	19.0751	38.0520	

TABLE 4.5 Simulated concentration for Potassium K^+ (1995)

n_H(mgmol/L)	Xm=0.15	Xm=0.20	Xm=0.25	
	θ_H=0.14	θ_H=0.18	θ_H=0.22	EXPERIMENTAL
	Cc(mg/L)	Cc(mg/L)	Cc(mg/L)	Cc(mg/L)
0.0000000794	1.2726×10^{-7}	2.63576×10^{-7}	5.41899×10^{-7}	2.00
0.1000000794	0.14129	0.3319	0.6825	
0.2000000794	0.2839	0.6639	1.3649	
0.3000000794	0.4259	0.9959	2.0475	
0.4000000794	0.5679	1.3278	2.7299	
0.5000000794	0.7098	1.6598	3.4124	
0.6000000794	0.8518	1.9917	4.0949	
0.7000000794	0.9938	2.3237	4.7774	
0.8000000794	1.1358	2.6557	5.4599	
0.9000000794	1.2777	2.9876	6.1424	

TABLE 4.6 Simulated concentration for Sodium Na^{+} (1995)

n_{H}(mgmol/L)	Xm=0.15	Xm=0.20	Xm=0.25	
	$\theta_{H}=0.14$	$\theta_{H}=0.18$	$\theta_{H}=0.22$	EXPERIMENTAL
	Cc(mg/L)	Cc(mg/L)	Cc(mg/L)	Cc(mg/L)
0.0000000794	6.64792×10^{-8}	1.5544×10^{-7}	$3.19581\times10^{-}$	1.50
0.1000000794	0.0837	0.1958	7	
0.2000000794	0.1675	0.3915	0.4024	
0.3000000794	0.2512	0.5873	0.8049	
0.4000000794	0.3349	0.7831	1.2075	
0.5000000794	0.4186	0.9788	1.6099	
0.6000000794	0.5024	1.1746	2.0124	
0.7000000794	0.5861	1.3703	2.4149	
0.8000000794	0.6698	1.5660	4.8175	
0.9000000794	0.7535	1.7619	3.2199	
			3.6225	

TABLE 4.7 Simulated concentration for Calcium Ca^{2+} (1995)

n_{H} (mgmol/L)	Xm=0.25	Xm=0.30	Xm=0.35	
	$\theta_{H}=0.22$	$\theta_{H}=0.26$	$\theta_{H}=0.30$	EXPERIMENTAL
	Cc(mg/L)	Cc(mg/L)	Cc(mg/L)	Cc(mg/L)
0.0000000794	5.5579×10^{-7}	1.085×10^{-6}	2.16583×10^{-6}	9.60
0.1000000794	0.6999	1.3674	2.7277	
0.2000000794	1.3999	2.7347	5.4555	
0.3000000794	2.0999	4.1022	8.1832	
0.4000000794	2.7999	5.4696	10.9109	
0.5000000794	3.4996	6.8369	13.6366	
0.6000000794	4.1999	8.2044	16.3664	
0.7000000794	4.8999	9.5717	19.0942	
0.8000000794	5.5999	10.9392	21.8219	
0.9000000794	6.2999	12.3065	24.5497	

TABLE 4.8 Simulated concentration for Magnesium Mg^{2+} (1995)

n_H (mgmol/L)	Xm=0.30	Xm=0.35	Xm=0.40	EXPERIMENTAL
	θ_H=0.26	θ_H=0.30	θ_H=0.34	
	Cc(mg/L)	Cc(mg/L)	Cc(mg/L)	Cc(mg/L)
0.0000000794	6.51428×10^{-7}	1.2990×10^{-6}	3.01079×10^{-6}	3.88
0.1000000794	0.8204	1.6366	3.7919	
0.2000000794	1.6408	3.2733	7.5838	
0.3000000794	2.4613	4.9099	11.3758	
0.4000000794	3.2818	6.5465	15.1677	
0.5000000794	4.1022	8.1832	18.9596	
0.6000000794	4.9226	9.8199	22.7515	
0.7000000794	5.7431	11.4565	26.5435	
0.8000000794	6.5635	13.0932	30.3354	
0.9000000794	7.3839	14.7298	34.1273	

4.13 Simulated RESULTS [Tungan Kawo Dam (1995)]

The results shown in table 4.9 to table 4.14.

TABLE 4.9 Simulated concentration for Phosphorous P^{3+} (1995)

n_H (mgmol/L)	Xm=0.05	Xm=0.10	Xm=0.15	
	θ_H=0.06	θ_H=0.10	θ_H=0.14	EXPERIMENTAL
	Ccmg/L	Ccmg/L	Ccmg/L	Ccmg/L
0.0000000501	4.0129×10^{-9}	2.3711×10^{-10}	6.75027×10^{-8}	0.02
0.1000000501	0.0080	0.0449	0.1347	
0.2000000501	0.0160	0.0899	0.2694	
0.3000000501	0.0240	0.1348	0.4694	
0.4000000501	0.0320	0.1798	0.5389	
0.5000000501	0.0400	0.2248	0.6736	
0.6000000501	0.0480	0.2697	0.8084	
0.7000000501	0.0561	0.3147	0.9432	
0.8000000501	0.0641	0.3596	1.0779	
0.9000000501	0.0721	0.4046	1.2126	

TABLE 4.10 Simulated concentration for Nitrogen (N^-) 1995.

n_H (mgmol/L)	Xm=0.15	Xm=0.20	Xm=0.25	
	$\theta_H=0.14$	$\theta_H=0.18$	$\theta_H=0.22$	EXPERIMENTAL
	Ccmg/L	Ccmg/L	Ccmg/L	Ccmg/L
0.0000000501	4.40544×10^{-8}	1.00135×10^{-7}	1.95798×10^{-7}	0.90
0.1000000501	0.0879	0.1998	0.3908	
0.2000000501	0.1758	0.3997	0.7816	
0.3000000501	0.2637	0.5996	1.1724	
0.4000000501	0.3517	0.7995	1.5632	
0.5000000501	0.4396	0.9993	1.9540	
0.6000000501	0.5276	1.1992	2.3448	
0.7000000501	0.6155	1.3991	2.7356	
0.8000000501	0.7034	1.5989	3.1265	
0.9000000501	0.7913	1.7988	3.5173	

TABLE 4.11 Simulated concentration for Potassium K^+ (1995).

n_H (mgmol/L)	Xm=0.35	Xm=0.40	Xm=0.45	
	$\theta_H=0.30$	$\theta_H=0.34$	$\theta_H=0.38$	EXPERIMENTAL
	Ccmg/L	Ccmg/L	Ccmg/L	Ccmg/L
0.0000000501	3.76122×10^{-7}	6.30007×10^{-7}	1.0715×10^{-6}	2.50
0.1000000501	0.7507	1.2575	2.1387	
0.2000000501	1.5015	2.5150	4.2774	
0.3000000501	2.2522	3.7725	6.4161	
0.4000000501	3.0030	5.0299	8.5549	
0.5000000501	3.7537	6.2875	10.6936	
0.6000000501	4.5045	7.5450	12.8323	
0.7000000501		8.8024	14.9710	
0.8000000501	5.2552	10.0599	17.1097	
0.9000000501	6.7567	11.3175	19.2484	

TABLE 4.12 Simulated concentration for Sodium Na^+ (1995)

N_H (mgmol/L)	Xm=0.40	Xm=0.45	Xm=0.50	
	θ_H=0.34	θ_H=0.38	θ_H=0.42	EXPERIMENTAL
	Ccmg/L	Ccmg/L	Ccmg/L	Ccmg/L
0.0000000501	3.7154×10^{-7}	6.31908×10^{-7}	1.14955×10^{-6}	
0.1000000501	0.7416	1.2611	2.2945	
0.2000000501	1.4832	2.5226	4.5890	
0.3000000501	2.2248	3.7839	6.8836	
0.4000000501	2.9664	5.0452	9.1781	2.50
0.5000000501	3.7080	6.3065	11.4726	
0.6000000501	4.4496	7.5678	13.7671	
0.7000000501	5.1912	8.8291	16.0616	
0.8000000501	5.9328	10.0903	18.3562	
0.9000000501	6.6744	11.3576	20.6507	

TABLE 4.13: Simulated Concentration For Calcium Ca^{+2} (1995)

n_H (mgmol/L)	Xm=0.45	Xm=0.50	Xm=0.55	
	θ_H=0.38	θ_H=0.42	θ_H=0.46	EXPERIMENTAL
	Ccmg/L	Ccmg/L	Ccmg/L	Ccmg/L
0.0000000501	1.0989×10^{-6}	1.99923×10^{-6}	4.42701×10^{-6}	
0.1000000501	2.1936			
0.2000000501	4.3871			
0.3000000501	6.5807			
0.4000000501	8.7742			16.00
0.5000000501	10.9678			
0.6000000501	13.1613			
0.7000000501	15.3549			
0.8000000501	17.5484			
0.9000000501	19.7419			

TABLE 4.14: Simulated Concentration For Magnesium Mg^{2+} (1995)

n_H (mgmol/L)	Xm=035	Xm=0.40	Xm=0.45	EXPERIMENTAL
	θ_H=0.3s	θ_H=0.34	θ_H=0.38	
	Ccmg/L	Ccmg/L	Ccmg/L	Ccmg/L
0.0000000501	2.3146×10^{-7}	3.8769×10^{-7}	6.5938×10^{-7}	6.80
0.1000000501	0.4199	0.7738	1.3161	
0.2000000501	0.9239	1.5476	2.6322	
0.3000000501	1.3859	2.3215	3.9483	
0.4000000501	1.8479	3.0953	5.2645	
0.5000000501	2.3099	3.8692	6.5806	
0.6000000501	2.7719	4.6430	7.8967	
0.7000000501	3.2339	5.4169	9.2129	
0.8000000501	3.6959	6.1907	10.5290	
0.9000000501	4.1579	6.9046	11.8452	

4.14 Simulated result [River Kaduna at Gusoro Awolu (2001)]

The result is shown below from table 4.15 to 4.19

TABLE 4.15: Simulated Concentration For Nitrogen N^{+} (2001)

n_H (mgmol/L)	Xm=0.40	Xm=0.45	Xm=0.50	
	θ_H=0.34	θ_H=0.38	θ_H=0.42	EXPERIMENTAL
	Ccmg/L	Ccmg/L	Ccmg/L	Ccmg/L
0.0000000501	1.0015×10^{-8}	1.7034×10^{-6}	3.0988×10^{-6}	24.00
0.1000000501	1.9991	3.4000	6.1852	
0.2000000501	3.9998	6.8000	12.3704	
0.3000000501	5.9982	10.2000	18.5556	
0.4000000501	7.9955	13.6000	24.7409	
0.5000000501	9.9955	17.0000	30.9261	
0.6000000501	11.9946	20.4000	37.1113	
0.7000000501	13.9937	23.8000	43.2966	
0.8000000501	15.9925	27.2000	49.4818	
0.9000000501	17.9914	30.6000	55.6670	

TABLE 4.16: Simulated Concentration For Potassium K^+ (2001)

n_H (mgmol/L)	Xm=0.15	Xm=0.20	Xm=0.25	
	θ_H=0.14	θ_H=0.18	θ_H=0.22	EXPERIMENTAL
	Ccmg/L	Ccmg/L	Ccmg/L	Ccmg/L
0.0000000501	2.7711×10^{-8}	6.2988×10^{-8}	1.2316×10^{-7}	0.26
0.1000000501	0.0553	0.1257	0.2458	
0.2000000501	0.1106	0.2515	0.49817	
0.3000000501	0.1657	0.3772	0.4375	
0.4000000501	0.2213	0.5029	0.9833	
0.5000000501	0.2766	0.6286	1.2292	
0.6000000501	0.3319	0.7544	1.4750	
0.7000000501	0.3872	0.8801	1.7208	
0.8000000501	0.4425	1.0058	1.9667	
0.9000000501	0.4978	1.1315	2.2125	

TABLE 4.17: Simulated Concentration For Sodium Na^+ (2001)

n_H (mgmol/L)	Xm=0.05	Xm=0.10	Xm=015	
	θ_H=0.06	θ_H=0.10	θ_H=0.14	EXPERIMENTAL
	Ccmg/L	Ccmg/L	Ccmg/L	Ccmg/L
0.0000000501	9.7156×10^{-10}	4.4536×10^{-9}	1.6343×10^{-8}	2.99×10^{-3}
0.1000000501	0.0019	0.0109	0.0326	
0.2000000501	0.0039	0.0218	0.0652	
0.3000000501	0.0058	0.0327	0.0979	
0.4000000501	0.0078	0.0435	0.1305	
0.5000000501	0.0097	0.0544	0.1631	
0.6000000501	0.0116	0.0653	0.1957	
0.7000000501	0.0136	0.0762	0.2283	
0.8000000501	0.0155	0.0871	0.2609	
0.9000000501	0.0175	0.0979	0.2936	

TABLE 4.18: Simulated Concentration For Caicium Ca^{+2}(2001)

n_H (mgmol/L)	Xm=0.45	Xm=0.50	Xm=055	EXPERIMENTAL
	θ_H=0.38	θ_H=0.42	θ_H=046	
	Ccmg/L	Ccmg/L	Ccmg/L	Ccmg/L
0.0000000501	1.0989×10^{-6}	1.9992×10^{-6}	4.2701×10^{-8}	40.00
0.1000000501	2.1936	3.9905	8.8363	
0.2000000501	4.3871	7.9809	17.6727	
0.3000000501	6.5807	11.9714	26.5090	
0.4000000501	8.7742	15.9624	35.3454	
0.5000000501	10.9678	19.9524	44.1817	
0.6000000501	13.1613	23.9428	53.0180	
0.7000000501	15.3549	27.9333	61.8544	
0.8000000501	17.5484	31.9238	70.6907	
0.9000000501	19.7419	35.9114	76.5271	

TABLE 4.19: Simulated Concentration For Magnesium Mg^{2+} (2001)

$_H$ (mgmol/L)	Xm=045	Xm=0.50	Xm=055	EXPERIMENTAL
	θ_H=0.38	θ_H=0.42	θ_H=0.46	
	Ccmg/L	Ccmg/L	Ccmg/L	Ccmg/L
0.0000000501	6.5938×10^{-7}	1.1995×10^{-6}	2.6562×10^{-6}	10.80
0.1000000501	1.3161	2.3943	5.3018	
0.2000000501	2.6323	4.7886	10.6036	
0.3000000501	3.9484	7.1828	15.9054	
0.4000000501	5.2645	9.5772	21.2072	
0.5000000501	6.5807	11.9714	26.5090	
0.6000000501	7.8968	14.3657	31.8108	
0.7000000501	9.2129	16.7599	37.1126	
0.8000000501	10.5291	19.1543	42.4144	
0.9000000501	11.8458	21.5485	47.7162	

4.14: Simulated Results [Tungan Kawo 2001]

The result is shown from 4.20 to4.20

TABLE 4.20 SIMULATED CONCENTRATION FOR NITROGEN N^+(2001)

n_H (mgmol/L)	Xm=0.45	Xm=0.50	Xm=055	
	θ_H=0.38	θ_H=0.42	θ_H=046	EXPERIMENTAL
	Ccmg/L	Ccmg/L	Ccmg/L	Ccmg/L
0.0000000398	7.1029×10^{-7}	1.1356×10^{-8}	1.8955×10^{-6}	22.00
0.1000000398	1.7847	2.8533	4.7624	
0.2000000398	3.5693	5.7066	9.5249	
0.3000000398	5.3539	8.5599	14.2873	
0.4000000398	7.1386	11.4132	19.0497	
0.5000000398	8.9233	14.2666	23.8122	
0.6000000398	10.7079	17.1199	28.5746	
0.7000000398	12.4926	19.9732	33.3370	
0.8000000398	14.2773	22.8265	38.0995	
0.9000000398	16.0619	25.6799	42.8619	

TABLE 4.21 Simulated Concentration For Potassium K^+(2001)

n_H (mgmol/L)	Xm=0.15	Xm=0.20	Xm=0.25	EXPERIMENTAL
	θ_H=0.14	θ_H=0.18	θ_H=0.22	
	Ccmg/L	Ccmg/L	Ccmg/L	Ccmg/L
0.0000000398	1.3821×10^{-8}	3.1273×10^{-8}	6.0344×10^{-8}	0.32
0.1000000398	0.0347	0.0784	0.1516	
0.2000000398	0.0695	0.1568	0.3032	
0.3000000398	0.1042	0.2352	0.4549	
0.4000000398	0.1389	0.3136	0.6065	
0.5000000398	0.1736	0.3921	0.7581	
0.6000000398	0.2084	0.4705	0.9097	
0.7000000398	0.2430	0.5489	1.0613	
0.8000000398	0.2778	0.6273	1.2129	
0.9000000398	0.3125	0.7057	1.3646	

TABLE 4.22 Simulated Concentration For Sodium Na^+(2001)

n_H (mgmol/L)	Xm=0.15	Xm=0.20	Xm=0.25	EXPERIMENTAL
	θ_H=0.14	θ_H=0.18	θ_H=0.22	
	Ccmg/L	Ccmg/L	Ccmg/L	Ccmg/L
0.0000000398	8.151×10^{-9}	$1.8405\times^{-8}$	3.5587×10^{-8}	0.21
0.1000000398	0.0204	0.0462	0.0894	
0.2000000398	0.0409	0.0925	0.1788	
0.3000000398	0.0614	0.1387	0.2682	
0.4000000398	0.0819	0.1849	0.3577	
0.5000000398	0.1024	0.2312	0.4471	
0.6000000398	0.1229	0.2775	0.5365	
0.7000000398	0.1434	0.3237	0.6259	
0.8000000398	0.1638	0.3699	0.7153	
0.9000000398	0.1843	0.4162	0.8047	

TABLE 4.23 Simulated Concentration For Calcium Ca^{2+}(2001)

n_H (mgmol/L)	Xm=0.55	Xm=0.60	Xm=0.65	EXPERIMENTAL
	θ_H=0. 46	θ_H=0.5	θ_H=0.54	
	Ccmg/L	Ccmg/L	Ccmg/L	Ccmg/L
0.0000000398	1.02229×10^{-6}	2.2777×10^{-6}	5.8973×10^{-6}	36.00
0.1000000398	3.0725	5.7229	14.8174	
0.2000000398	6.1451	11.4458	29.6348	
0.3000000398	9.2116	17.1687	44.2523	
0.4000000398	12.2901	22.8916	59.2697	
0.5000000398	15.3627	28.6145	74.0807	
0.6000000398	18.4352	34.3376	88.9046	
0.7000000398	21.5078	40.0603	103.7219	
0.8000000398	24.5803	45.7832	108.5393	
0.9000000398	27.6528	51.5061	133.3568	

TABLE 4.24 Simulated Concentration For Magnesium Mg^{2+}(2001)

n_H (mgmol/L)	Xm=0.45	Xm=0.5	Xm=0.55	EXPERIMENTAL
	θ_H=0.38	θ_H=0.42	θ_H=0.46	
	Ccmg/L	Ccmg/L	Ccmg/L	Ccmg/L
0.0000000398	2.7495×10^{-7}	4.3959×10^{-7}	7.3372×10^{-7}	9.60
0.1000000398	0.6908	1.1045	1.8435	
0.2000000398	1.3817	2.2090	3.6870	
0.3000000398	2.0725	3.3135	5.5306	
0.4000000398	2.7633	4.4180	7.3741	
0.5000000398	3.4542	5.5226	9.2176	
0.6000000398	4.1450	6.6271	11.0611	
0.7000000398	4.8359	7.7316	12.9047	
0.8000000398	5.5257	8.8361	14.7482	
0.9000000398	6.2175	9.9406	16.5917	

The tables below are for figure 1 and 2. for NO_3^+ and K^+ respectively.

Table 4.25: NO_3^+

Sites	Experimental	Simulated
1	24	23.8
2	22	22.82
3	9.01	9.02
4	15.65	15.34
5	27.5	23.3
6	6.75	7
7	12.66	12.61

Table 4.26: K^+

Sites	Experimental	Simulated
1	0.26	0.251
2	0.32	0.313
3	0.41	0.392
4	0.37	0.372
5	0.19	0.13
6	0.42	0.4203
7	0.46	0.4602

4.1.2 DISCUSSION OF RESULT

This model predicts the concentration of cations present in soil water. Based on the rate of reaction of parent rock (weathering).

The fraction (Xm) of the cation was varied and its three different fraction was considered for each site. Also, three different θ_H (adsorption sites occupied by H^+) were also considered. And three different predictive concentrations of cations each was obtain to check on the corresponding values that tally with experimental value. And this predictive value of concentrations depends on the range of Xm and θ_H. The simulated value shown in Table 4.3 to 4.24.

Two sites were considered only for the simulation each for 1995 and 2001 were about twenty-two table were generated. And these sites are River Kaduna at Gusoro/Awolu and Tungan Kawo.

Considering 1995 the simulated values for each cations was in table 4.3 to 4.8 for the first site River Kaduna at pH 7.1and also for the second site Tungan Kawo at pH 7.3 was presented in table 4.9 to 4.14.

Also, for 2001 the simulated value for cations for the first site River Kaduna was presented in table 4.15 to 4.19 and the second site Tungan Kawo was also presented in table 4.20 – to – 4.24.

Table 4.3 shows the simulated concentration of Phosphorus where n_H was varied from 0.00000000.794 to 0.90000000794 and from the table it shows that the simulated result is reasonably close with the experimental at fractions Xm = 0.05, θ_H = 0.06 and n_H = 0.10000000794 or 0.20000000794.

Table 4.4 the simulated result for Nitrogen gives a slight variation also, With that of the experimental. Where the simulated value is at Xm= 0.30, θ_H 0.26 and n_H at 0.7000000794. For the 4.5 the simulated value 1.99mg/L at Xm = 0.20 θ_H = 0.18 and nH at 0.6000000794 is almost close to the experimental value which is 2.0mg/L. Table 4.6 also shows a slight difference with that of the experimental and the simulated value at Xm = 0.2, θ_H = 0.18 and n_H = 0.8000000794. Table 4.7 gives also a very close range of value of experimental 9.6mg/l and that of simulated 9.57177mg/L at fractions Xm = 30, θ_H = 0.26 and n_H = 0.70000000794. Also table 4.8 shows a slight discrepancies in the values of Experimental value 3.88mg/l and the simulated value of magnesium 3.7919mg/l at Xm 0.40 θ_H = 0.34 and n_H is at 0.10000000794. This reasonable closeness might be due to assumption of the fractions made.

The simulated result for Tungan Kawo Dam 1995 at pH = 7.10. Where again each cations were tabulated from table 4.9 to 4.14.

~~The~~ table 4.9 showed a significant variation between the experimental and the simulated value of P^{3+} at Xm = 0.05, θ_H= 0.06 and n_H = 0.3000000501.

Table 4.11 and 4.12 shows a very reasonable closeness in their values. Table 4.1.1 which simulate the concentration of Potassium at Xm = 0.40, θ_H = 0.34 and at n_H = 0.2000000501 while table 4.12 which simulate the concentration of sodium at Xm = 0.45 and θ_H 20.38 and also n_H = 0.2000000501. And which both the cations (sodium and potassium) has the experimental concentration values of 2.5mg/c. This gives them same effect on usability UGS water supply paper 1964)

Table 4.13 shows the simulated concentration of calcium at Xm = 0.50, θ_H = 0.42 and n_H at 0.4000000501 shows a difference in a minimal range with that of experimental. This closeness can be concluded that they are almost the same.

Table 4.14 the simulated concentration of Mg^{2+} at Xm =0.4, θ_H = 0.34 and n_H = 0.9000000501. shows a significant closeness with the experimental result.

For the 2001 the simulated result for River Kaduna of pH = 7.30 where each cation under this site were tabulated from table 4.15 – 4.19. For table 4.15 the simulated result of concentration of Nitrogen 23.80006 at Xm 0.45, θ_H = 0.38 and n_H =0.000000501 gives a very reasonable closeness in range with the experimental which is 24.0mg/l.

In addition, table 4.16 shows the slight variations of experimental value of potassium with the simulated value at Xm = 0.2, θ_H = 0.18 and n_H = 0.2000000501. Moreover, table 4.17 shows the simulated concentration for sodium vat at Xm = 0.05, θ_H = 0.06 and n_H = 0.300000501 showed a slight variation with the experimental value. For the table 4.18 the simulated concentration for calcium at Xm = 0.55 and θ_H = 0.46 and the n_H = 0.5000000501 showed a very wide variation with the experimental value with difference of about 4.18170 which very high.

This wide difference might be as result of the assumptions made in the process of the model.

Table 4.19 also shows the concentration for magnesium simulated at Xm = 0.55, θ_H = 0.46 and 0.2000000501 which shows a reasonable closeness with the experimental value.

The simulated results for Tungan Kawo 2001 at pH 7.40 where each cation under this site are tabulated.

For table 4.20 the simulated concentration of Nitrogen at Xm = 0.5, θ_H = 0.42 at n_H = 0.8000000398 which is compared with the experimental value shows a slight variation. For table 4.21 which shows the concentration of Potassium simulated at Xm = 0.2, θ_H = 0.18 and n_H = 0.400000398 which showed there is slight variations in range with the experimental. Table 4.22 also shows a close variations between the experimental and simulated value of concentration of sodium at Xm = 0.20, θ_H = 0.18 and at n_H = 0.5000000598. Table 4.23 shows the simulated concentration for calcium at Xm = 0.6, θ_H = 0.5 and n_H = 0.600000398 shows a wide variation in range of concentration with the experimental. And table 2.24 shows the simulated concentration of magnesium at Xm = 0.5, θ_H = 0.42 and n_H = 0.9000000398 which gives a reasonable closeness with the experimental value. The similarities is simulated values presented in the tables can be attributed to the fact that the rate of dissolution of these mineral from the bedrock mineral to the soil is very slow (Nahon, 1991).

The discrepancies between the year 1995 and 2001 might be due to the facts that the year difference is very wide. Irregular carrying out of the irrigation water and soil sampling attributes this. Since the programme is supposed to be carried out seasonally which will be beneficial and profitable to various irrigation schemes, and more importantly to the rural communities. Report on dry season irrigation water sampling and analysis for quality control and management by (J.A. Oladipo 1995) upper river Basin Minna.

Also the changes in cations concentration in irrigated farmland is insignificantly influenced by the weathering of parent rocks. Certain concentration changes is therefore as a result of external influences (Adeniyi, 2001). And generally, the figures 1 and 2 show the difference in respect to the whole sites.

The variation between experimental and the simulated result could be due to the following factors.

1. The variation in experimental and simulated values could be attributed to some of the assumption made in developing of the model. One is that the fractions (Xm) occupied by cation in a site and the adsorption site

occupied by H^+ which are varied arbitrarily and also the reaction temperature of 25°C considered for the soil might not conform to the prevailing soil temperature it is known fact that ion solubility is a function of temperature.

2. The variation could also be, because of the large difference in years for the experimental results. That is from 1995 to 2001.
3. In addition, assumption that soil is clay might not be true completely as it might be a mixture of clay and some other types of soil.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

From this research, the following conclusions can be deduced.

1. Solubility of the cations applied to soil depends on their mineral form grain or granules sizes and on soil condition particularly moisture content and pH. Interaction among the cations presents in soil and removal by leaching, plants and living organisms.
2. It is dependent on the nutrient added to the soil, in the form of fertilizers.
3. The research work on modelling of concentration of cations that is sodium, magnesium, phosphorus, potassium, nitrogen gives us an insight into the relationship between experimental data and equation in varying the performance of the data.
4. In addition, the model to a good extent showed the contribution of weathering process to the soil cation concentration.

5.2 RECOMMENDATION

Based on some observation in the of this research work, the following recommendation were made.

1. this project work can be extended to other industries such as steel rolling industries ,they discharges waste water and is further recycled for further use in the industry .so this model will enable them determined level of concentrations present in the water.
2. This research work can also apply to other ions considered in the river basin but not considered in this research.

It is also recommended that further research on the subject matter should be extended in order to determine the mole of each of the ions specifically which will enable or enhances the determination of their concentrations rather than considering the mole as a whole in a particular site.

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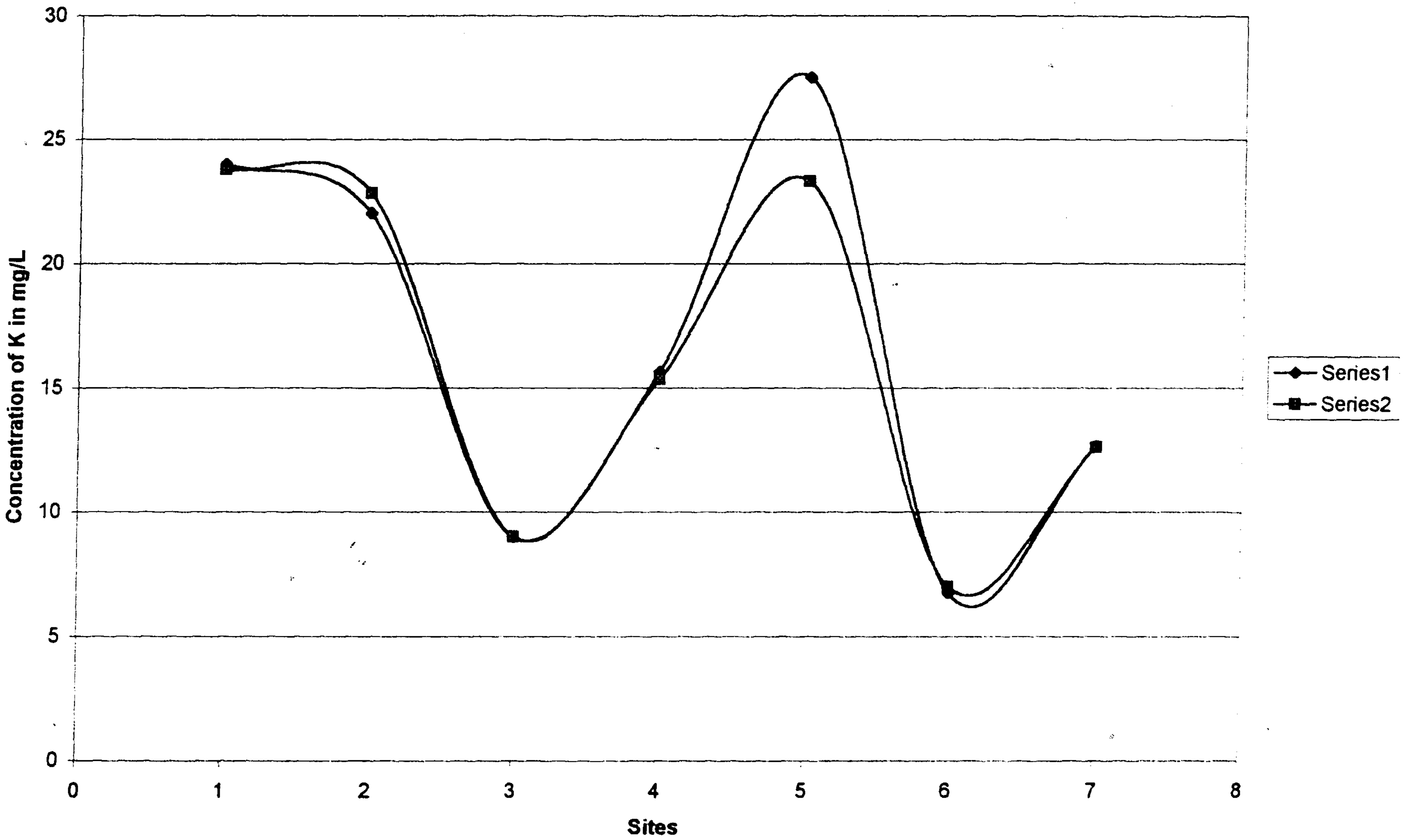
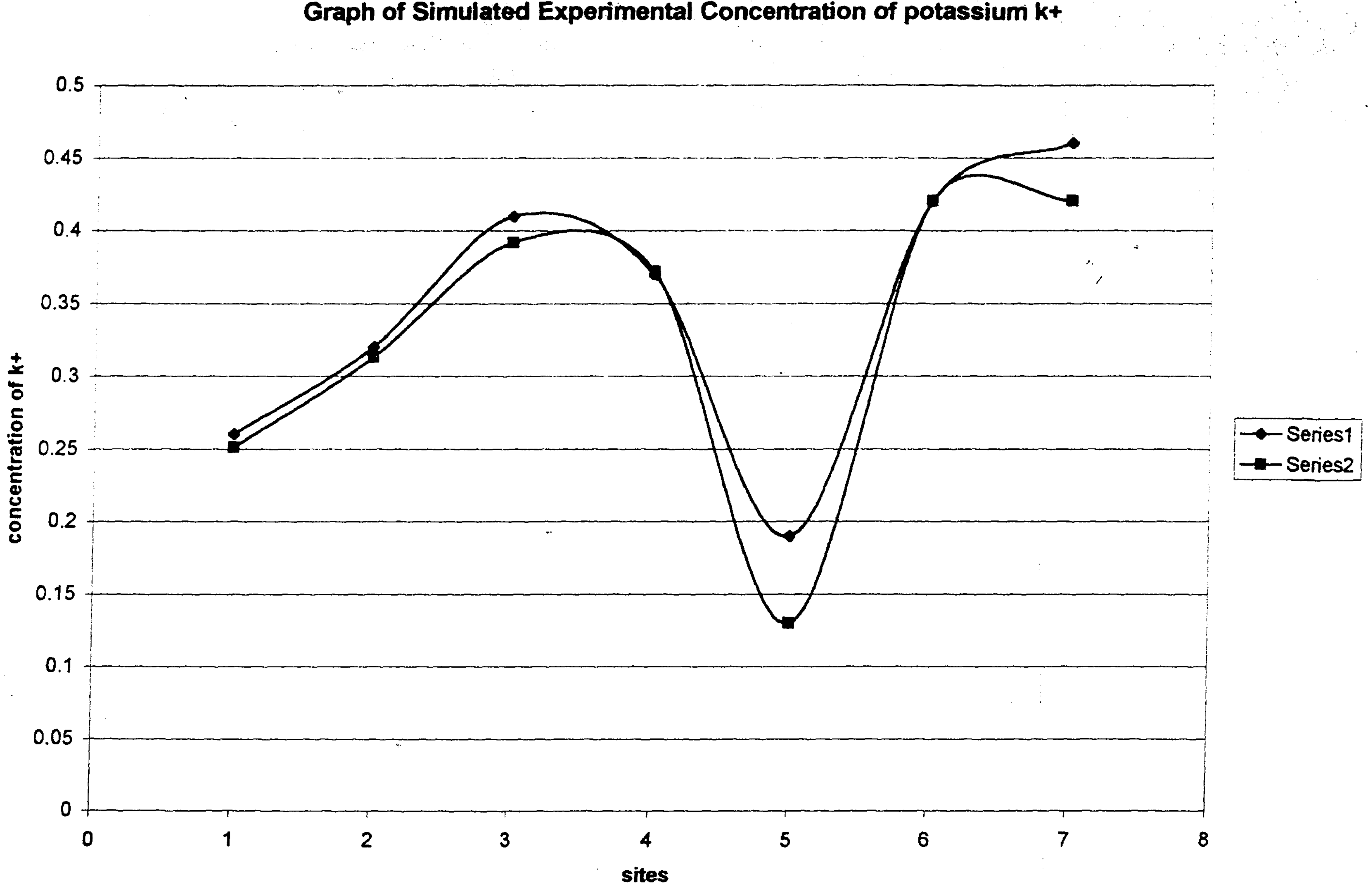
APPENDIX

Graph of Experimental and Simulated Concentration of N+




Graph of Simulated Experimental Concentration of potassium k+
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
concentration of k+
0
1
2
3
4
5
6
7
8
sites
Series1
Series2