



Development of Model for the Prediction of Ions Concentration in Soil Water

O. D. ADENIYI

Department of Chemical Engineering, Federal University of Technology, Minna, Nigeria

lekanadeniyi2002@yahoo.co.uk

Abstract

This paper proposes a mathematical model for the prediction of different ion concentration in soil water used for irrigational purposes in Niger State of Nigeria. The various ions considered are sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), nitrogen in form of nitrate (NO_3^-), and phosphorus in form of phosphate (PO_4^{3-}). The model was simulated for different concentration readings using different adsorption fractions. The results obtained compared favourably with that of the experimental, though with slight variations which were attributed to some of the basic assumptions used during the process of model development.

Keywords

Ions, Concentration, Adsorption, Site, Simulation

1. Introduction

It is a know fact that 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 supply 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. The important sources of chloride however are from sewage and intruded sea water. Occasionally nitrate 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 ground water by solution (Jackson and Sherman, 1953; Lasaga, 1981a; Nahon, 1991).

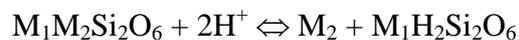
The water passing through igneous rocks dissolves only very small quantities of mineral matter because of the relative insolubility of the rock composition percolating rainwater contain carbon dioxide (CO₂) derived from the atmosphere, which increases the solvent action of water. The silicate mineral of igneous rocks result in silica being added to the ground. Pyroxenes are solid solution of great complexity all of which have the basic formula XY [(Si, Al)O₃]₂ where X maybe Na⁺, Ca²⁺, Mn²⁺, Fe²⁺, and Li⁺ and Y maybe Mn²⁺, Fe²⁺, Mg²⁺, Fe³⁺, Al³⁺, Cr³⁺, and Ti⁴⁺ (Schott and Petit, 1987; Nahon, 1991).

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 contains salt concentrations several times that of the applied irrigation water, increases result from evapotranspiration process, which tends to concentrate salts in drainage. In addition, soluble soil materials, fertilizers and selective absorption of salts by plants will modify salt concentration of percolating water. Factors governing the increase include; soil permeability, drainage facilities, amount of water applied, crops and climates. CO₂ in solution derived from the atmosphere and from organic processes in soil, assist the solvent action of water as it moves underground. Ordinarily, high concentrations of dissolved constituents are found in groundwater than in surface water because of the greater materials in geologic strata (Todd, 1980). In the lower part of the soil strata and deeper in the ground, the dissolved compounds in water consist mostly of carbonate, sulphate, calcium, magnesium, sodium, and potassium ions with usually small amount of chloride, iron and silica. Commonly dissolved gases include carbon dioxide, nitrogen, oxygen, methane, and hydrogen sulphide (Nahon, 1991; Adeniyi 2001). This paper proposes a mathematical model developed for the prediction of ions concentration in irrigational soil water.

2. Exchange Reaction

The framework of silicate minerals follow the rule of electron neutrality, the surface of these minerals displays atoms and ions with incompletely saturated valances. Therefore, in contact with water, charged surface allow polarisation of water molecules and hence separation, at the mineral-solution interface, of the H₂O dipoles into H⁺ and OH⁻ through the respective attraction on non saturated negative and positive charges of the surface of the crystal. The H⁺ proton attaches itself to one or several water molecules and from a hydronium ion H₃O⁺. The H⁺ proton with its very small diameter and monovalent charge generates a very strong attraction on the oxygen ions of the surface of the crystal. Thus development of these chemical reactions between substrate and adsorbate generates chemisorption for which corresponding adsorption heats are about ten times greater than for a simple physical adsorption generating Van Der Waals forces (Touray, 1980).

Chemisorption is accompanied by a substitution of Ca²⁺, Na⁺, K⁺ cations whose attraction with respect to the oxygen of the crystalline structure is weaker because of their large diameter (Touray, 1980; Perry and Green, 1997). Following Lasaga (1981b) and taking as an example the weathering of pyroxene, Schott and Berner (Nahon, 1991) proposed chemisorption and substitution reactions for the surface reaction by the equation:



The progressive rate of reaction can be set as:

$$r^+ = dnM_2 / dt = k^+ x_{m2} \theta_H^2 \quad (1)$$

With θ_H expressed in Langmiur isotherm:

$$K = \theta_H / (m_H - \theta_H) \quad (2)$$

$$x_{m2} = 1 - x_H \quad (3)$$

where θ_H - fraction of the adsorption site occupied by H⁺; θ_E - fraction of the adsorption site vacant; x_{m2} = fraction of the surface of M₂ site occupied by M₂ cations; K - equilibrium constant for adsorption; m_H - concentration of H⁺ in the solution x_{m2} and x_H can be expressed as a function of the number of moles of M₂ cations (n_{M2px}) and of hydrogen (n_{Hpx}) contained in the M₂ sites of the surface of the pyroxene with the expression:

$$n_{px} = n_{M2px} + n_{Hpx} \quad (4)$$

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

$$n_{Hpx} = n_{M2s} - n_{M1s} \quad (5)$$

where n_{M2s} and n_{M1s} are the number of moles of cations released in solution from sites M_1 and M_2 , Schott and Berner (Nahon, 1991) reached the following expression:

$$r^+ = k_+ K^2 \theta_E^2 m_H^2 - k_+ K^2 \theta_E^2 m_H^2 \frac{(n_{M2s} - n_{M1s})}{n_{px}} \quad (6)$$

Using the above equations, Adeniyi (2001) proposes a model for the concentration of ions in soil relative to H^+ as M_H given by the equation:

$$M_H = \frac{K \theta_E \sqrt{\left(1 - \frac{n_{Hpx}}{n_{px}}\right)}}{x_{m2}^{0.5} \theta_H} \quad (7)$$

From Equation 7 we have:

$$M_H x_{m2}^{0.5} = K \theta_E \sqrt{\left(1 - \frac{n_{Hpx}}{n_{px}}\right)} \quad (8)$$

$$\frac{M_H x_{m2}^{0.5}}{K \theta_E} = \sqrt{\left(1 - \frac{n_{Hpx}}{n_{px}}\right)} \quad (9)$$

Squaring both sides of equation 9,

$$\left(\frac{M_H \theta_H}{K \theta_E}\right)^2 x_{m2} = 1 - \frac{n_{Hpx}}{n_{px}} \quad (10)$$

$$1 - \left(\frac{M_H \theta_H}{K \theta_E}\right)^2 x_{m2} = \frac{n_{Hpx}}{n_{px}} \quad (11)$$

$$\frac{n_{Hpx}}{n_{px}} = \frac{K^2 \theta_E^2 - M_H^2 \theta_H^2 x_{m2}}{K^2 \theta_E^2} \quad (12)$$

$$\frac{n_{px}}{n_{Hpx}} = \frac{K^2 \theta_E^2}{K^2 \theta_E^2 - M_H^2 \theta_H^2 x_{m2}} \quad (13)$$

$$n_{px} = \frac{n_{Hpx} K^2 \theta_E^2}{K^2 \theta_E^2 - M_H^2 \theta_H^2 x_{m2}} \quad (14)$$

Substituting equation 4 into 14, we obtain:

$$n_{m2px} + n_{Hpx} = \frac{n_{Hpx} K^2 \theta_E^2}{K^2 \theta_E^2 - M_H^2 \theta_H^2 x_{m2}} \quad (15)$$

$$n_{m2px} = \frac{n_{Hpx} K^2 \theta_E^2}{K^2 \theta_E^2 - M_H^2 \theta_H^2 x_{m2}} - n_{Hpx} \quad (16)$$

$$n_{m2px} = \frac{n_{Hpx} K^2 \theta_E^2 - n_{Hpx} K^2 \theta_E^2 + n_{Hpx} M_H^2 \theta_H^2 x_{m2}}{K^2 \theta_E^2 - M_H^2 \theta_H^2 x_{m2}} \quad (17)$$

$$n_{m2px} = \frac{n_{Hpx} M_H^2 \theta_H^2 x_{m2}}{K^2 \theta_E^2 - M_H^2 \theta_H^2 x_{m2}} \quad (18)$$

Equation 18 gives the model for the moles of ion in a given soil medium and thus the concentration of the ions can be determined by multiplying the moles by its molecular weight (M_{wt}) so that the equation can be written as:

$$C_{ion} = n_{m2px} M_{wt} \quad (19)$$

$$C_{ion} = \frac{n_{Hpx} M_{wt} M_H^2 \theta_H^2 x_{m2}}{K^2 \theta_E^2 - M_H^2 \theta_H^2 x_{m2}} \quad (20)$$

Equation 20 gives the required model for the prediction of the concentration of a given ion in soil water.

3. Results and Discussion

The experimental results obtained for the concentration of some ions for seven different sites for the year 1995 and 2001 are presented in tables 1 and 2. The simulated results are presented in tables 3-6 while the comparison of two different ions is given in figures 1 and 2.

Table 1. Experimental results of soil water analysis in mg/L for 1995

Site	1	2	3	4	5	6	7
Source	River Kaduna at Gusoro Awolu	Tungan Kawo Dam	River Gurara at Izom	River Tafa at New Wuse	Swashi Dam	River Galma at Igabi	River Galma at Zaria
pH	7.10	7.30	7.30	7.20	7.30	7.10	7.20
PO ₄ ³⁻	0.30	0.02	0.00	0.00	0.01	0.00	0.00
NO ₃ ⁻	14.50	0.90	3.00	14.50	6.00	10.00	7.00
K ⁺	2.00	2.50	2.00	2.50	1.00	1.00	2.50
Na ⁺	1.50	2.50	1.50	1.00	0.50	3.00	0.50
Ca ²⁺	9.60	16.00	8.00	9.60	16.00	17.60	17.60
Mg ²⁺	3.88	6.80	5.82	5.82	4.85	6.80	5.82

Table 2. Experimental results of soil water analysis in mg/L for 2001

Site	1	2	3	4	5	6	7
pH	7.30	7.40	7.40	7.00	7.50	6.70	7.00
PO ₄ ³⁻	-	-	-	-	-	-	-
NO ₃ ⁻	24.000	22.000	9.010	15.650	27.500	6.750	12.660
K ⁺	0.260	0.320	0.410	0.370	0.190	0.420	0.460
Na ⁺	0.003	0.210	0.095	0.060	0.090	0.610	0.190
Ca ²⁺	40.000	36.000	20.000	16.000	28.000	16.000	38.000
Mg ²⁺	10.800	9.600	10.800	6.000	15.600	3.600	8.400

Table 3. Simulated concentration (mg/L) for N⁺

n _{Hpx}	River Kaduna at Gusoro Awolu		Tunga Kawo Dam	
	1995	2001	1995	2001
0.1000000794	2.1195	3.4000	0.1998	2.8533
0.2000000794	4.2389	6.8000	0.3997	5.9066
0.3000000794	6.3584	10.2000	0.5996	8.5599
0.4000000794	8.4779	13.6000	0.7995	11.4132
0.5000000794	10.5973	17.0000	0.9993	14.2666
0.6000000794	12.7168	20.4000	1.1992	17.1199
0.7000000794	14.8363	23.8000	1.3991	19.9732
0.8000000794	16.9537	27.2000	1.5989	22.8265
0.9000000794	19.0751	30.6000	1.7988	25.6799

Table 4. Simulated concentration (mg/L) for Na⁺

n _{Hpx}	River Kaduna at Gusoro Awolu		Tunga Kawo Dam	
	1995	2001	1995	2001
0.1000000794	0.1958	0.0019	1.2611	0.0462
0.2000000794	0.3915	0.0039	2.5226	0.0925
0.3000000794	0.5873	0.0058	3.7839	0.1387
0.4000000794	0.7831	0.0078	5.0452	0.1849
0.5000000794	0.9788	0.0097	6.3065	0.2312
0.6000000794	1.1746	0.0116	7.5678	0.2775
0.7000000794	1.3703	0.0136	8.8291	0.3237
0.8000000794	1.5660	0.0155	10.0903	0.3699
0.9000000794	1.7019	0.0175	11.3576	0.4162

Table 5. Simulated concentration (mg/L) for Ca²⁺

n _{Hpx}	River Kaduna at Gusoro Awolu		Tunga Kawo Dam	
	1995	2001	1995	2001
0.1000000794	1.3674	8.8363	2.1936	5.7229
0.2000000794	2.7347	17.6727	4.3871	11.4458
0.3000000794	4.1022	26.5090	6.5807	17.1687
0.4000000794	5.4696	35.3454	8.7742	22.8916
0.5000000794	6.8369	44.1817	10.9678	28.6145
0.6000000794	8.2044	53.0180	13.1613	34.3376
0.7000000794	9.5717	61.8544	15.3549	40.0603
0.8000000794	10.9392	70.6907	17.5484	45.7833
0.9000000794	12.3065	76.5271	19.7419	51.5061

Table 6. Simulated concentration (mg/L) for Mg²⁺

$n_{H_{px}}$	River Kaduna at Gusoro Awolu		Tunga Kawo Dam	
	1995	2001	1995	2001
0.1000000794	0.8204	1.3161	0.7738	1.1045
0.2000000794	1.6408	2.6323	1.5476	2.2090
0.3000000794	2.4613	3.9484	2.3215	3.3135
0.4000000794	3.2818	5.2645	3.0953	4.4180
0.5000000794	4.1022	6.5807	3.8692	5.5226
0.6000000794	4.9226	7.8968	4.6430	6.6271
0.7000000794	5.7431	9.2129	5.4169	7.7316
0.8000000794	6.5635	10.5291	6.1907	8.8361
0.9000000794	7.3839	11.8458	6.9046	9.9406

The model developed was simulated using varying fraction of ion (x_{m2}) as well as the adsorption site occupied by H^+ (θ_H). The experimental results from seven different sites are presented in tables 1 and 2 for two different years (1995 and 2001). The sites considered are from Niger State of Nigeria (fig. 3). The seven sites considered in this work are from various streams and dam used for irrigational purposes. The observed lowest pH value for 1995 was 7.10 while that of 2001 was 6.70. It is notable that in the year 2001 the test for phosphate ions could not be carried out due to some problems with the analytical equipment and not that there was no presence of phosphate in the water sample, this is part of the major advantage that this model gives, it allow for the prediction of the various ions. It is observed from tables 1 and 2 that the readings of 2001 are fairly higher than that of 1995, the reason attributed to this was that there were accumulation of various ions in the soil as a result of continuous fertilizer application within the soil over the years (Odigure and Adeniyi, 2003a, b).

Simulated nitrogen ion concentrations are presented in table 3 for the two years and two sites under consideration. The obtained concentration for River Kaduna was higher than those for Tunga Kawo dam for the two years. The inferred reason was attributed to the facts that River Kaduna flows from a neighbouring state brings along with it various concentration from different sites. It could also be due to the level of farming activities at that time (Odigure and Adeniyi, 2003b). The number of moles of ion contributed as a result of weathering was taken from 0.1000000794 to 0.9000000794 for all the simulated values.

Table 4 present the simulated concentration for sodium ion, it was observed that the ion concentration for 1995 were higher than that of 2001 for the first site and similar pattern for the second site. The changes in ion concentration in irrigated farmland are insignificantly influenced by the weathering of parent rock (Nahon, 1991). Certain concentration changes are

therefore as a result of external influences (Adeniyi 2001; Odigire and Adeniyi, 2003a). Other reasons are adsorption and precipitation processes (Bordas and Bourg, 2001) because the geochemical processes responsible for the exchange of metals at the water-sediment interface are adsorption and precipitation (Mouret and Bourg, 1983; Salomons and Förster, 1984; Wang et-al, 1997). The two mechanisms are greatly dependent on pH (Bourg and Loch, 1995).

The simulated results for calcium is given in table 5, the value for the year 1995 was higher than those of the year 2001 for the two sites considered. The same pattern was noticed fore magnesium ion (table 6). The comparisons of experimental and simulated results are presented in figs. 1 and 2.

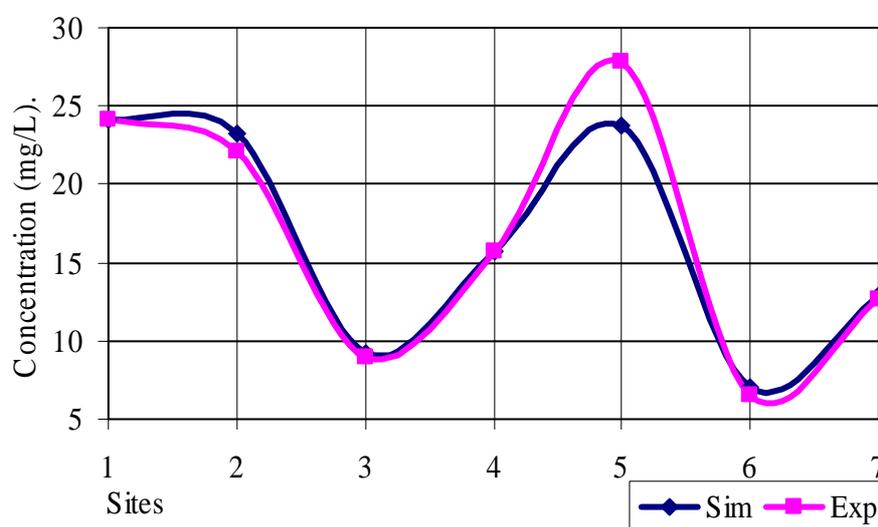


Fig. 1. Experimental and simulated concentration of NO_3^-

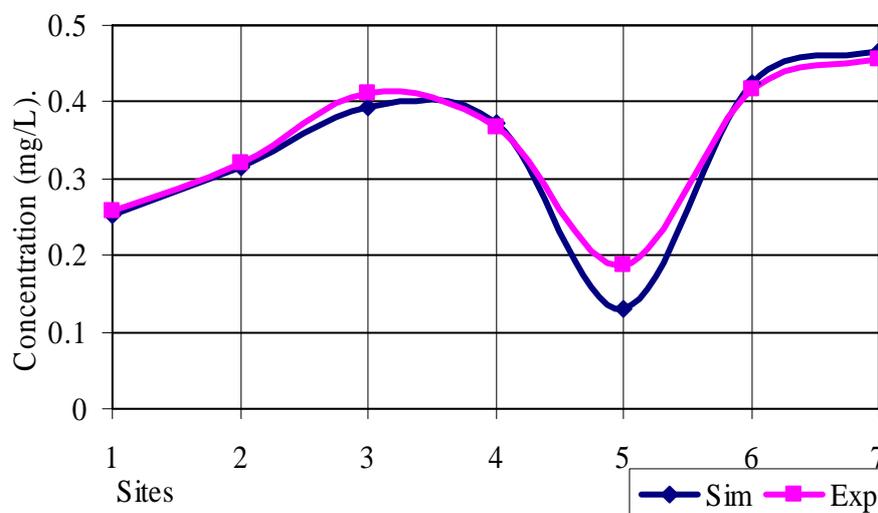


Fig. 2. Experimental and simulated concentration of K^+

The two results follow a similar pattern but with slight difference. From fig. 1 at the fifth site there is a large deviation in the concentration between the simulated and experimental while in fig. 2 this deviation was noticed at the third and fifth sites.

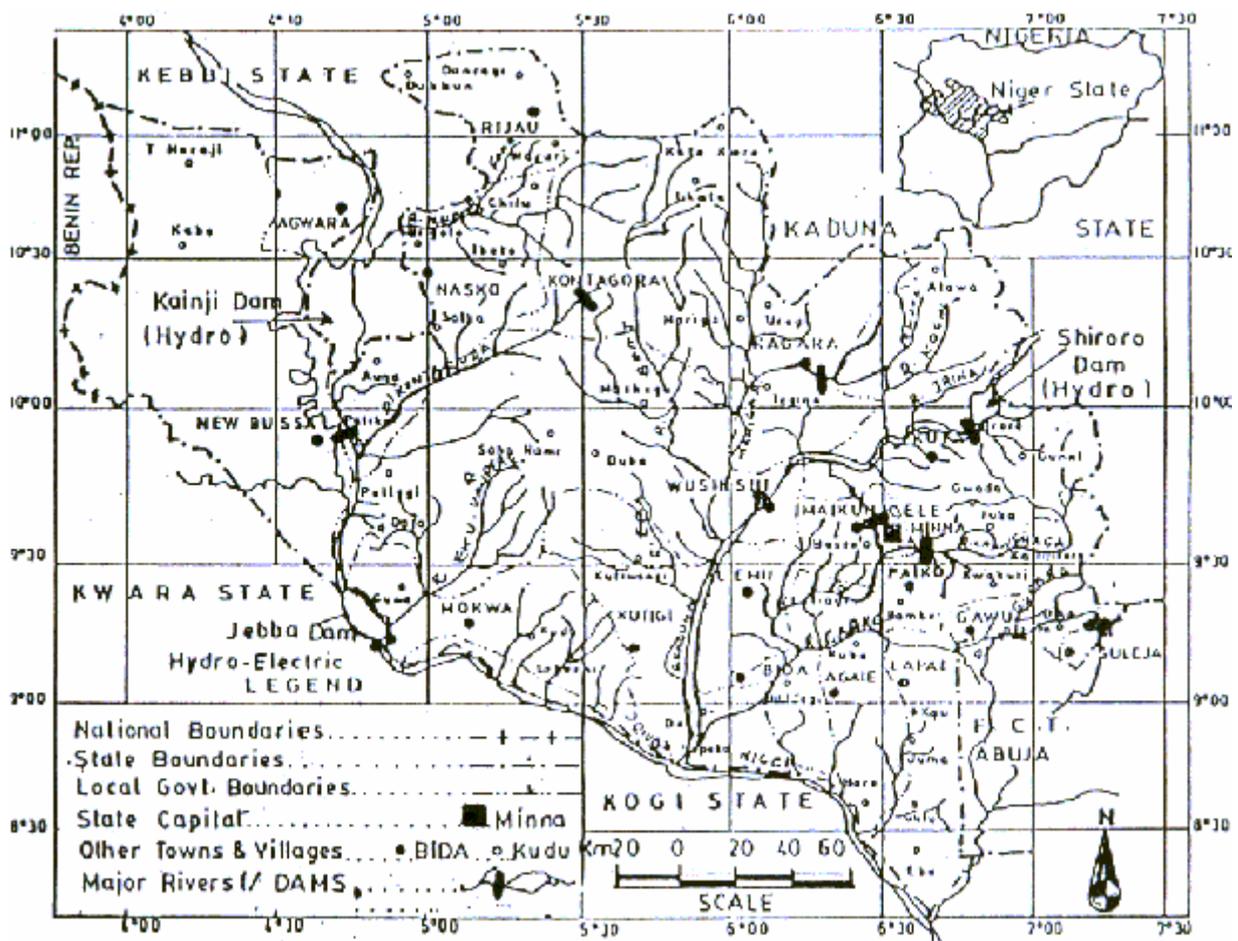


Fig. 3. Map of Niger State of Nigeria

The variation between experimental and simulated values could be attributed to some of the assumption made in developing the model. One is that the fraction (x_{m2}) occupied by the ion in a site and the adsorption site occupied by the hydrogen ion (θ_H) were varied arbitrarily. Another reason could be the selection of soil temperature of 25°C used in calculating the soil equilibrium constant which might not conform to the prevailing soil temperature and it is a known fact that ion solubility is a function of temperature (Nahon, 1991; Odigure and Adeniyi, 2003a).

Conclusions

The model developed was simulated for different concentration readings using different adsorption fractions. The results obtained compared favourably with that of the experimental, though with slight variations, which, were attributed to some of the basic assumptions used during the process of model development. The level of the ion concentration was observed to depend on the solubility of the ions, their mineral form and on the soil conditions of particular interest are the temperature, the moisture content and pH. This research work on modelling of the various ions gives an insight into the depletion of the various ions in the soil medium.

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