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Modelling C - 2003

Mathematical Modelling of Cathion Retention
in Soil Water from Various Sites

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Abstract

Weathering and fertilizer applications are two factors responsible for the contribution of minerals to soil water. As a result of chemical reactions within the soil and in the presence of excess water, most of these minerals could be ionized in aqueous solutions, and leached/ transferred to other area. This paper proposes some mathematical models based on empirical data that can be used to predict the concentration of cations in soil water from various areas. The proposed model gives a predictive value of the concentration of a cation as a function of prevailing pH and the concentration of other ions present in a given soil water. The comparative analysis of simulation and experimental values from various sites for the year 1991/92 showed some disparities while that of 1991/95 was close. This could be attributed to the facts that, within 1991/92 a lot of farming activities were probably accompanied with the application of fertilizers to the land, thus, the concentration of these cations varied sharply from those of simulated values. On the other hand, farming activities in 1995 was at its minimum relative to 1991.

Keywords

Modeling, nitrogen (N), phosphorus (P) and potassium (K), sodium (Na), Hydrogen (H), pH

1. Introduction

Soil is a living entity, it is subject to depletion of its nutrients, however, the rate of depletion is a function of the soil type, rate of ion exchange and the rate of introduction of fresh nutrients. Mineral weathering and organic matter decomposition are two processes, which contribute new inorganic and organic materials to soil profiles. Man mimics these inputs with additions of inorganic fertilizers and organic manures (Nahon, 1991; Ross, 1989; Hunt, 1972). Fertilizer consists of three basic elements, which are required in

different quantities by plants. These elements are nitrogen (N), phosphorus (P) and potassium (K). The nitrogen available in the atmosphere is gaseous and in this natural state cannot be used by plants, thereby nitrogen must be process into urea to fix it into soluble form, which can be used by plants. Phosphorus occurs in nature as an insoluble phosphate rock. These rocks are crushed and treated with acids to form phosphate salts i.e. super phosphate rock. These phosphate salts are not easily soluble. They are sometimes further treated with ammonia to form monoammonium phosphate (MAP, $NH_4H_2PO_4$) and diammonuim phosphate (DAP, $(NH_4)_2HPO_4$), which are soluble and easily absorbed by the plants. Potassium is also found as a rock in their natural state. These also are crushed and treated with various chemicals and acids to form the muriate of potash (MOP, K_2SO_4), which is highly soluble form of potassium and is easily absorbed (Adeniyi, 2001; Perry and Green, 1997).

2. Methodology

2.1 Pretreatment of Water Samples

On arrival from each field trip, water samples already collected in white plastic containers were kept in an air-conditioned room to maintain the room temperature, which did not exceed 25°C. The idea of doing this was purposely to reduce microbial activities, as much as possible, to the barest minimum. Immediately sampling was over and pretreatment accomplished, waste samples were conveyed to the laboratory for series of chemical analysis (Adeniyi, 2001; Adewole et al, 1995; Anderson, 1991).

2.2 Determination of pH

The pH meter was calibrated with pH 7.0 and pH 4.0 buffer solutions before use. The electrodes were rinsed with deionized water and with the samples to be analyzed. The electrodes of the pH meter were then inserted into the partly settled suspension and the pH measured out, without stirring the suspension during measurement. The electrodes were then rinsed with deionized water and wiped dried with a clean tissue after each reading (Anderson, 1991; Midgley and Torrance, 1991; Black, 1965; Jackson, 1962).

2.3 Determination of Potassium (K) and Sodium (Na)

The apparatus used was the flame photometry, the K and Na standards were 100 ppm both in aqueous solution.

2.3.1 Range of Standard Solutions

1. K standard – 0,2,4,6,8,10 ppm K, or 0,5,10,15,20, ppm K or 0,10,20,30,40 ppm K
   This depended on the concentration of K present in the sample solution, high concentration range of 0 to 100 ppm K was used for high K concentration.

2. Na standards – 0,2,4,6,8,10 ppm Na

2.3.2 Procedure

Flame photometer was set up according to instructions provided. The instrument readout was calibrated using the standard solutions. The meter was set at zero while aspiring distilled water of blank solution and set at 100 % E (Emission) while aspiring top concentration of standards. The %E reading of all the intermediate standard solutions was recorded and a standard curve on linear graph solution was recorded and the concentration of the element in the sample solution from the standard curve was read.

2.4 Determination of Nitrate

This involved the use of electrophotometer in which 1 ml of the sample was transferred to a vial and mixed. 0.5 ml brucine reagent was added then 2 ml of sulphuric acid was rapidly added. This was mixed for about 30 seconds and allowed to stand for 5 minutes. This was mixed again with the addition of 2 ml distilled water and continuous mixing for another 30 seconds. The tubes were set in cold water for about 5 minutes and the transmittance at 470 mμ was measured (Midgley and Torrance, 1991; Kreshkov, 1976; Black, 1965; Jackson, 1962).

2.5 Determination of Phosphorus (P)

This analysis involved the use of B & L spectronic –70 (electrophotocolorimetric). Two reagents A and B were prepared for the analysis.

2.5.1 Reagent A

12 g of ammonium molybdate $[(NH_4)_6Mo_7O_{24}]$ were dissolved in 250 ml of distilled water. Also 0.2908 g of potassium antimony tartarate $(KSbOC_4H_4O_6)$ was dissolved in

100ml of distilled water. 5N H_2SO_4 was prepared by diluting approximately 148 ml of concentrated H_2SO_4 in about 1000ml of distilled water. The solutions were mixed together in 2-litre volumetric flask and made up to volume with distilled water.

2.5.2 Reagent B

1.056 g of ascorbic acid was dissolved to every 200 ml of reagent A.

2.5.3. Procedure

2 to 5 ml of the sample was pipetted into 25ml volumetric flask or a marked test tube, with 10 ml of distilled water added. 4 ml of reagent B was added and made up to volume with distilled water. The colour was allowed to develop for 15 minutes and the P content in solution was determined on the spectrophotometer at 882 mμ (Midgley and Torrance, 1991; Anderson, 1991; Kreshkov, 1976).

3. Regression Model

These models were obtained by the linear regression of the experimental data using the software "Polymath" of Himmelblau (1987). The model gives predictive values of H^+, P^+, N^+, K^+ and Na^+ as a function of the nine cations considered. The models are given as follows:

$$H = 4.75771 \times 10^{-8} + 4.4797 \times 10^{-6}P - 2.03289 \times 10^{-7}N + 2.0621 \times 10^{-7}K + 1.30257 \times$$
$$10^{-7}Na - 2.87445 \times 10^{-7}Ca + 3.68302 \times 10^{-7}Mg + 4.422 \times 10^{-5}Fe -$$
$$0.000856308Mn + 4.01949 \times 10^{-5}Zn \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

$$P = 0.256209 - 0.0350165 \, pH + 0.034464N - 0.00825062K - 0.0125063Na +$$
$$0.0793352Ca - 0.108922Mg - 10.1259Fe + 200.86Mn - 0.53935Zn \quad \ldots\ldots\ldots 2$$
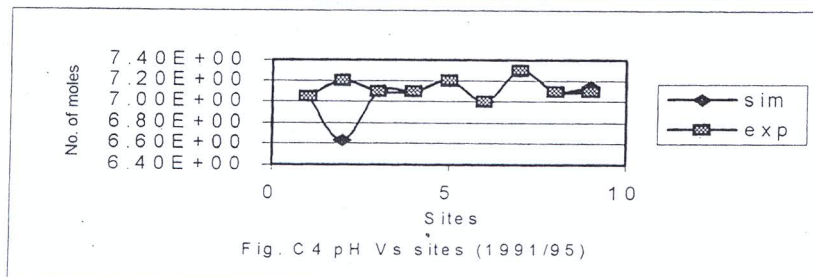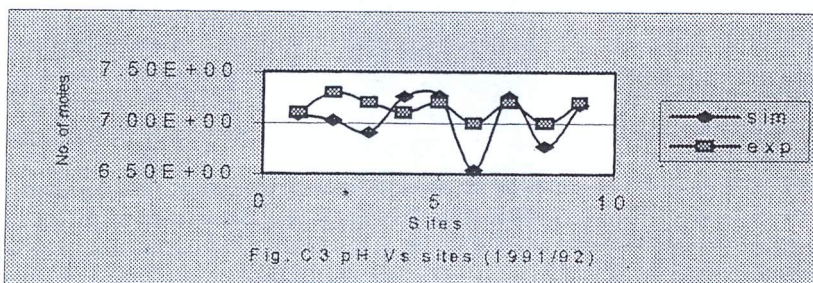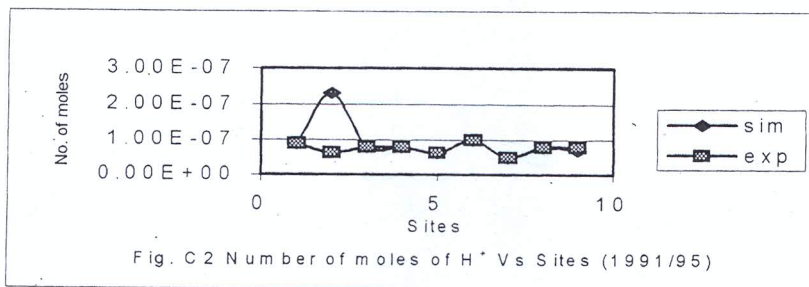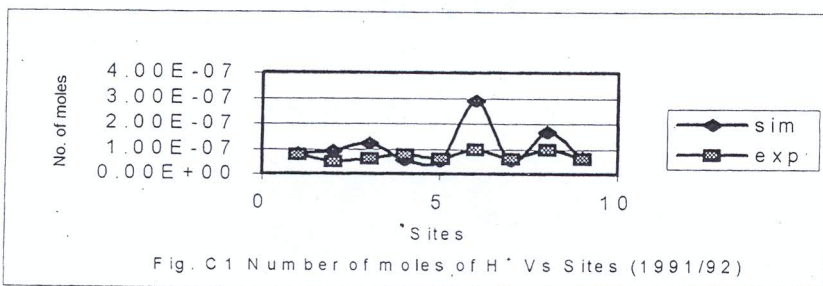
$$N = -7.43412 + 1.01603pH + 29.0158P + 0.239398K + 0.36288Na - 2.30198Ca +$$
$$3.16046Mg + 293.811Fe + 24344.8 \, Mn + 276.792Zn \quad \ldots\ldots\ldots\ldots\ldots\ldots 3$$

$$K = 31.0534 - 4.2441pH - 121.203P + 4.17714N - 1.5158Na + 9.61567Ca - 13.2017Mg$$
$$- 1227.29Fe + 24344.8Mn - 1156.2Zn \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

$$Na = 20.4865 - 2.79991pH - 79.9599P + 2.75573N - 0.659718K + 6.34363Ca -$$
$$8.7094Mg - 809.666Fe + 16060.7Mn - 762.765Zn \quad \ldots\ldots\ldots\ldots\ldots\ldots 5$$

4. Results

The obtained results for both simulation and experimental are given in Figs. C1-C12 below.

Fig. C1 Number of moles of H⁺ Vs Sites (1991/92)

Fig. C2 Number of moles of H⁺ Vs Sites (1991/95)

Fig. C3 pH Vs sites (1991/92)
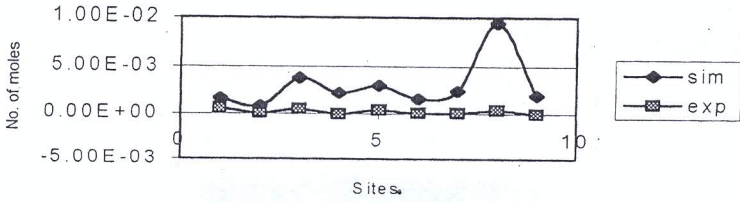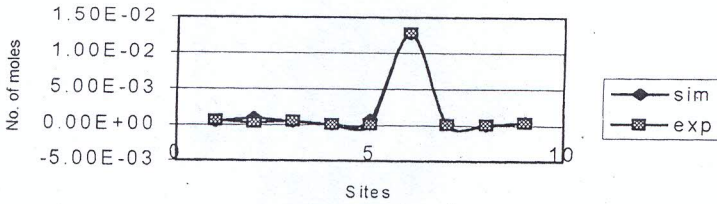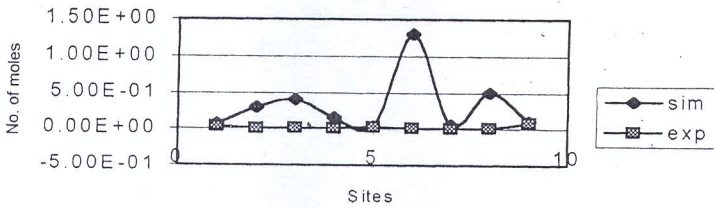

Fig. C4 pH Vs sites (1991/95)

Fig. C5 Number of moles of P^{3+} vs sites (1991/92)

Fig. C6 Number of moles of P^{3+} vs sites (1991/95)
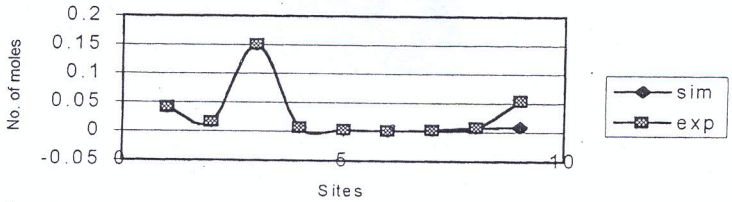

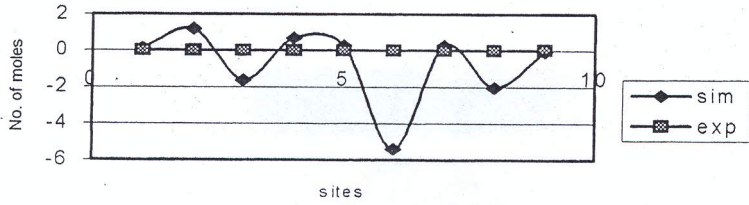Fig. C7 Number of moles of N^+ vs sites (1991/92)

Fig. C8 Number of moles of N^+ vs sites (1991/95)

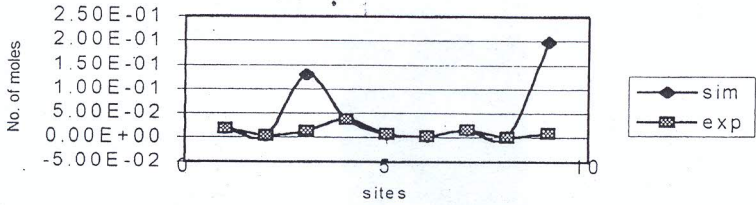Fig. C9 Number of moles of K⁺ vs sites (1991/92)

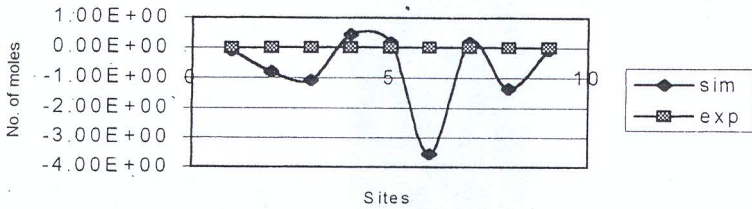Fig. C10 Number of moles of K⁺ vs sites (1991/95)
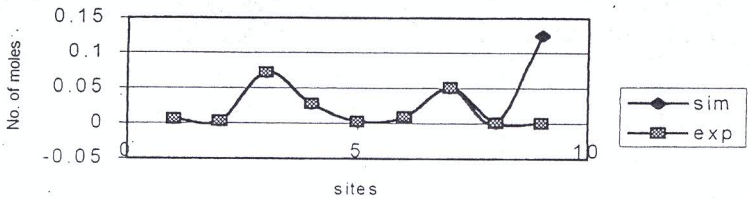

Fig. C11 Number of moles of Na⁺ vs sites (1991/92)

Fig. C12 Number of moles of Na⁺ vs sites (1991/95)

5.0 Discussion

Analysis results were collected from nine different sites around Niger State, Nigeria (Fig. C13). These nine sites are: Kerawa small earth dam at Kerawa; Fatika small earth dam at Fatika ; River Galma at Igabi ; River Kaduna at Kagoro ; River Niger at Shonga ; River Gbako at Agaie; Tunga Kawo dam at Tunga Kawo ; Nasko earth dam at Nasko ; and Rijau dam at Jama'are.

The results of the simulated and experimental values are presented in Figs. C1 to C12. For 1991/92 the simulated pH values (using equation 1) for the nine sites were close to the experimental value. A little deviation was noticed for that of River Galma, the simulated pH value was 6.81 and experiment value was 7.2. The biggest deviations in values were observed for River Gbako, with a simulated value of 4.6 and an experimental value of 7.0. This could be attributed to the fact that the amount of fertilizers applied to a given soil need not follow a uniform pattern for each farming season; it is dependent on the extent of cropping (Adeniyi, 2001).

The simulated and experimental values for the year 1991/95 (Fig. C2 to C12) show a remarkable agreement with each other for all the nine sites considered. This confirms that the amount of cations and anions in the soil is predominantly dependent on the extent of fertilizer application and farming activities (Odigure and Adeniyi, 2001; Nahon, 1991).

Equation 1 presents the relationship between the numbers of mole of H^+ against the number of moles of other nine cations. A good correlation of the model and experiment was observed in both the H^+ and pH values for the year 1991/95 (8.91×10^{-8} mg/l and 7.05). The only exception was in Fatika dam with H^+ for both simulated and experiment at 2.33×10^{-7} mg/l and 6.31×10^{-8} mg/l and pH at 6.63 and 7.2 respectively. For the year 1991/92, the sharpest deviation was observed at River Galma with value of H^+ at 2.91×10^{-7} mg/l and 1.0×10^{-7} mg/l for both simulated and experimental. Also there was a sharp difference between Nasko with H^+ at 1.68×10^{-7} mg/l and 1.0×10^{-7} mg/l and pH of 6.77 and 7.0 respectively for simulated and experimental.

Figures C5 to C12 represents the graphs of the simulated and experimental values of nine cations concentration versus the sites under investigation. There is a sharp difference between the simulated and experimental nitrogen values (Fig. C7) for 1991/92, with the simulated values predominantly higher in most sites. It is well known that ammonium nitrogen is predominantly introduced to the soil via NPK fertilizer application. It could be retained in soils for long periods of time if conditions for nitrification are unfavourable (Tisdale and Nelson, 1975). The cationic nature of ammonium nitrogen (NH_4^+) permits its adsorption and retention by soil colloidal material. It is less easily removed by leaching compared to the nitrate form. Nitrate nitrogen is completely mobile in soils and within limits moves largely with the soil water. Both ammonium nitrogen and nitrate nitrogen can be immobilized by soil microflora (Tisdale and Nelson, 1975) e.g. blue-green algae and Rhodospirillum. Consequently leaching of ammonium commonly founding NPK fertilizer in the irrigated sites of Fatika, R. Galma, R. Gbako and Nasko can occur easily.

In 1991/92 (for phosphorus) the differences between simulated and experimental were high while the 1991/95 values show a remarkable close agreement (Fig. C5 and C6). It should be noted that the experimental P^{3+} values for most sites showed an increase between 1991 and 1995. Observed P^{3+} depletion might be connected to increased human farming activities in 1991. The presence of hydrous oxides of iron and aluminum also contributes to retention of added phosphorus, these compounds are found in soils containing large amount of 1:1 clay. Soil pH also affect phosphorus utilization, in most soils, phosphorus availability is at a maximum in the pH range of 5.5 to 7.0, decreasing as the pH drops below and above this range (Tisdale and Nelson, 1975).

6. Conclusion

The proposed model gives a predictive value of the concentration of a cation as a function of prevailing pH and the concentration of other ions present in a given soil water. The comparative analysis of simulation and experimental values from various sites for the year 1991/92 showed some disparities while that of 1991/95 was close. This could be attributed to the facts that, within 1991/92 a lot of farming activities were probably

accompanied with the application of fertilizers to the land, thus, the concentration of these cations varied sharply from those of simulated values. On the other hand, farming activities in 1995 was at its minimum relative to 1991.

7. References

Adeniyi O. D. " *Mathematical modeling and simulation of cation depletion in soil water*" M.Eng. Project, Federal University of Technology, Minna, Nigeria, pp1-127, 2001

Anderson R. "*Sample treatment and separation*", John Wiley & Sons Inc., Great Britain, 1991

Adewole A.O., Oladipo J.A., and Folowosele O.B. "*Dry season irrigation water sampling and analysis for quality control and management,*" Handbook, Upper Niger River Basin Development Authority, Minna, Nigeria, pp. 1-15, 1995

Black C. A. " *Methods of soil analysis,*" Agronomy No. 9 Part 2, Amer. Soc. Agronomy, Madison, Wisconsin, 1965

Himmelblau D.M. "*Basic Principles And Calculations In Chemical Engineering*" , 3rd ed., Prentice-Hill Inc., Englewood Cliffes, New Jersey, 1987.

Hunt C. B. "*Geology of soil–their evolution, classification and uses,*" Freeman & Co. Publication, San Francisco, 1972.

Jackson M. L. "*Soil Chemical analysis,*" Prentice Hall, New York, 1962

Kreshkov A.P. "*Basis of analytical chemistry*" 4th ed., Ximiya, Moscow, Vol. 1, 1976

Midgley D. and Torrance K. "*Potentiometric water analysis,*" 2nd ed., John Wiley and Sons, England, 1991

Nahon D.B. "*Introduction To The Petrology Of Soil And Chemical Weathering*", John Wiley & Sons Inc., France, pp 1-49,1991

Odigure J. O. and Adeniyi O.D. "*Mathematical modeling of weathering processes to ions in soil water*" A.M.S.E., Lyon, France, 2001

Perry R.H. and Green D.W. "*Perry's chemical engineers handbook,*" 7th ed., McGraw Hill Book Co., New York, 1997.

Ross S. "*Soil processes: A systematic approach,*" Routledge, Chapman and Hall Inc.,

New York, 1989.

Tisdale S.L. and W.L. Nelson *Soil Fertility And Fertilizers*, 3rd Edition,

Macmillan Publishing Co., Inc, New York ,1975

8. Acknowledgement

Fig. C13 Geological Map of Niger State, Nigeria

REFERENCE

SUPERFACIAL DEPOSITS

BIDA SANDSTONES

GRANITE & RELATED ROCKS

MIGMATITE-GNEISS + SCHISTS

INTERNATIONAL BOUNDARY ....

STATE BOUNDARY ....

STATE CAPITAL

LOCAL GOVT HEADQUARTERS...

OTHER TOWNS/VILLAGES

SCALE 1:1,000,000
ONE CENTIMETRE TO 10 KILOMETRES

GEO. LOGICAL KEY

Modelling

Measurement

& Control

C

ENERGETICS, CHEMISTRY & CHEMICAL ENGINEERING,
EARTH, RESOURCES, ENVIRONMENT
BIOMEDICAL PROBLEMS

IN MEMORIAM OF PROFESSOR G. MESNARD, FOUNDING MEMBER OF AMSE.