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MODELS FOR EVALUATING THE EFFECTS OF VARIATIONS IN pH OF RAIN WATER ON THE LEACHING OF FERTILIZER COMPONENTS IN SOILS

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ABSTRACT

Data from leaching experiments were used to develop mathematical models suitable for predicting the effects of the pH of rainwater on the leaching of major and minor components of applied fertilizer in different soils. The results show that for potassium (K) and calcium (Ca), there is a linear relationship with negative slope between the pH of leaching water and quantity of leached cation from applied fertilizer, for sodium the relationship is also linear but with a positive slope, while the quantity of nitrogen leached is independent of pH. In the case of phosphorus (P) the relationship is quadratic ie $C_p = \alpha pH + \beta(pH^2) - k$, whereas magnesium (Mg) shows a modified exponential relationship i.e of the form: $C_{Mg} = k - Q10^{-pH.B}$ where α, β, k, and Q are constants. For the two soils investigated, the models obtained for each component are identical in form showing that the coefficients of the equations could serve as quantitative indices for characterizing soils.

KEYWORDS: models, leaching, fertilizer components, linear, quadratic, modified exponential

INTRODUCTION

Operators of fertilizer bulk blending plants require ready access to accurate and reliable data on the characteristics of the soils for which their formulations are intended (Polley, 1990). Of special concern in this respect is the need to establish the patterns of distribution of fertilizer components when applied in the target soils.

Although the distribution of chemical matter in soils is brought about by processes such as erosion, runoff, plant intake, etc, the major pathways for the downward transportation of chemicals from the soil into the substrata is the leaching action of rain and irrigation water. Of the various leaching studies reported in the literature (Sanchez 1976, IITA 1983, Schofield et al, 1993 and Mageson et al, 1994), most have dealt with the issue of annual losses due to leaching of selected cations and anions in response to actual or simulated annual rainfall. These studies have been restricted to soil within the first 30cm from the surface (top soil), which is the region of utmost concern to agriculturists. Little or no attention has been given to the leaching effects in the sub-soil layers. Yet the inclusion of the substrata in leaching studies is important from environmental considerations, especially in view of the observations that quite a large number of underground waters are polluted with fertilizer components, especially nitrates and phosphates (Ozoemenam, 1992 and Faust and Aly 1998).

The acidity (pH) of rainwater is attributed to the interactions between the rainwater and atmospheric air, principally CO_2, (and SO_2, NO_2, H_2S and carbonates if present). It is known that the pH of rainwater depends on the season, location as well as anthropogenic activities in the area. For example, recent studies show that in the Niger-Delta Zone of Southern Nigeria, the pH of rainwater varies between values of 3.2 – 8.5 across the area, and between 3.2 and 6.15 over the year in one particular locality of Western Delta (Environmental Resource Managers Ltd, 1999). There is therefore the need to understand how these variations in the pH of rainwater affect the leaching of the components of applied fertilizer in soils.

There is paucity of information in the literature regarding effects of rainwater pH on the leaching of chemicals in soils and hence there is as yet no reliable basis for making precise and accurate predictions of the effects of the pH of rainwater on the leaching tendencies of the fertilizer chemicals in soil composites.

To fill this gap therefore, in vitro experiments have been conducted to investigate the relationships between the pH of input water (as lea chant) and the quantities of major and minor components of NPK fertilizer i.e. N, P, K and Ca, Na, Mg respectively, leached from fertilizer-treated agricultural and engineering soils respectively (Atkinson and Bransby, 1982).

EXPERIMENTAL

Sampling and Characterization of Soils

Samples of two soils were collected, one being farmland soil taken from a 'control plot' at National Root Crops Research Institute, Umudike in Abia State of Nigeria (labelled UCS for 'Umudike Control Soil'), and the other engineering soil or subsoil taken from Okigwe in Imo State of Nigeria. This was collected eight meters below the ground surface at a point that was freshly excavated for road construction and labelled OES (for 'Okigwe Engineering Soil').

Mechanical/Physical Analyses

The proportions of gravel, sand, silt and clay were determined by the Bouyoucous hydrometer method (Bouyoucous, 1951) and moisture content by the oven drying method (Udo and Ogunwale, 1978).

Chemical Analyses

Organic carbon and organic matter contents were obtained by the Walkley-Black Oxidation method and soil pH by using the Kent EIL model 7055 pH meter. N was determined by the standard Kjeldahl method and available phosphorus by the Bray–2 method using Spectronic 21 spectrophotometer at 660nm.

Cation exchange capacity was determined by the Ammonium solution method, exchangeable acidity and exchangeable Al by the potassium chloride extraction method. Exchangeable K, Na, Ca and Mg were extracted into 1 M Ammonium acetate; K, Na and Ca were determined by flame photometry using the Jenway flame photometer and Mg by EDTA titration.

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Details of the experimental procedures in the above analyses were, as provided in Udo and Ogunwale (1978, 1986).

Further, samples of the soils prepared by drying and sieving as above were than subjected to leaching experiments as described below.

Leaching Experiments

Each leaching water sample (leachant) used in the experiments was prepared by bubbling CO_2 from a Kipp's apparatus into distilled water until the water attained the desired pH values. Six bulk solutions ranging in pH between 4 and 7 were thus prepared as needed, labelled and used for the experimentation.

The leaching columns were prepared in pairs. Each pair consisted of two leaching tubes packed with pre-weighed quantities of identical soil (ie either UCS or OES). One column (the test column) was topped with a 1:1 mixture of silica glass and 1 gm of 15:15 NPK fertilizer obtained from NAAFCON, while the other column (the blank) was topped with silica glass only.

To make a leaching run, a selected leachant was passed down a selected column while maintaining a constant liquid head above the soil column in the tube. 100 ml of each leachant was collected, filtered and labeled.

The leaching exercise was repeated until freshly-prepared leachant (1 – 6) had passed through the freshly-prepared test and blank column pairs for the UCS and OES soils.

The experimental design used in these studies is summarized in Table 1.

Finally, the collected leach ate samples, (identified as $UCSF_1$ – $UCSF_6$, UCS_1- UCS_6, $OESF_1$ – $OESF_6$ and OES_1- OES_6 respectively) were analyzed for K, Ca, Na, Mg, N and P using the flame photometer for K, Na, Ca, EDTA titration for Mg, the Kjeldahl method for N and the Bray – 2 method for P as was used for soils earlier. Measurements were performed directly on the filtered leach ate in place of the soils or soil extracts.

TABLE 1: Experimental Parameters Used In The Leaching Studies

Identity and serial no of column/ leach ate	Mass of soil in column Kg x 10^{-3}	Length of soil column mm	Mass of fertilizer Kg x 10^{-3}	Thickness of fertilizer silica glass mm	Thickness of silica glass mm	Volume leach ate collected $m^3 \times 10^{-6}$	pH of leach ate (serial nos 1-6)
UCSF 1-6				15			1 - 4.31
	25	75					2 - 4.70
UCSW 1-6							3 - 5.10
			1.00	-	15	100	4 - 5.50
							5 - 6.41
OESF 1-6				15			6 - 6.76
		60			15		
OESW 1-6							

RESULTS AND DISCUSSION

The results obtained from these experiments are presented as follows:

Characteristics of the Soils

The mechanical, physical and chemical characteristics of the soils (UCS and OES) are tabulated in Table 2.

These results show that the UCS soil may be classified as clay soil while the OES soil is classified as sandy clay loam soil (USDA, 1951). The UCS soil is low in N,K, Ca, Mg, Al and in natural soil pH; however it has medium P and high organic matter content (Aduayi, *et al*, 2002) . The OES is lower in N, K, Ca, Mg Al, P, organic content, but of a higher soil pH (6.0 as against 4.0) than the UCS soil.

Flow Measurements

The recorded times for collecting 100cm^3 of the leachates are shown in Table 3. The figures have been used to evaluate the average flow rate of fluid through the columns and the flow rate data are also included in Table 3.

Leachate Compositions

The concentrations of the fertilizer constitutents of interest in the 100cm^3 of leach ate recovered are shown in Table 4.

Treatment of Data

To derive mathematical equations which describe the relationship between the quantity of each component leached and the pH of the leachant, the data of Table 4 were subjected to statistical analysis.

For K, Ca, Na and N, the problem was resolved by linear regression. For P and Mg, however, more rigorous search methods were investigated. The most successful technique involved the use of a numerical method based on analytical geometry (Crow et al, 1960; Dorn and McCracken, 1972), whereby a smooth curve was first drawn through a scatter plot of the C - pH data of Table 4 for any selected species/soil. Tangents were taken at various points along the curve at known values of pH and the valves of ($\partial C/\partial$ pH) plotted against pH. From the nature of the line of best fit drawn through these points, the mathematical relationship between C and pH was resolved.

TABLE 2: Physico-chemical Characteristics of the Soil Samples UCS And OES

(a) Mechanical Analysis of soils UCS and OES

Parameter (%)	UCS	OES
Gravel	1.2	Negligible
Sand	21.0	74.2
Silt	10.8	4.2
Clay	67.0	21.6
Moisture	29.0	6.0

(b) Chemical Properties of Soils UCS and OES

Parameter	UCS	OES
Organic Carbon, %	0.84	0.155
Organic matter, %	1.44	0.28
Soil pH	4.50	6.00
Exchangeable acidity, mmol/100g soil	5.70	3.10
Exchangeable Al mmol/100 soil	1.14	0.67
Magnesium mmol/100g soil	0.30	0.10
Sodium mmol/100g soil		
Potassium mmol/100g soil	0.12	0.08
Calcium mmol/100g soil	0.625	0.025
Cation exchange capacity mmol/100g soil	7.75	3.89
Phosphorus mg/L	16.5	5.0
Total N, %	0.115	0.06

TABLE 3: FLOW DATA FOR THE LEACHING EXPERIMENTS

Volume of fluid passed/collected = $100 \times 10^{-6} m^3$

Diameter of leaching tube = 10.0mm

Sample	Average leaching time (h)	Average fluid flow rate through column, V ($\times 10^{-5} m^3 h^{-1}$)
$UCSF_{1-6}$	7.74 ± 0.03	1.29
$UCSW_{1-6}$	7.69 ± 0.05	1.30
$OESF_{1-6}$	0.65 ± 0.04	15.4
$OESW_{1-6}$	0.58 ± 0.04	17.2

Table 4: CONCENTRATIONS OF FERTILIZER COMPONENTS IN THE LEACHATES C

	LEACHANT	1	2	3	4	5	6
	pH	4.31	4.70	5.10	5.50	6.40	6.76
COMPONENT	SOIL IDENTITY						
K mmol/ l	UCSF	14.46	13.39	12.36	10.88	10.56	9.27
	UCSW	0.072	0.066	0.073	0.075	0.082	0.06
	OESF	11.86	11.33	10.3	10.3	9.24	8.26
	OESW	0.042	0.041	0.038	0.041	0.042	0.039
Ca mmol/l	UCSF	0.81	0.77	0.60	0.60	0.56	0.505
	UCSW	0.13	0.13	0.13	0.11	0.12	0.13
	OESF	0.53	0.51	0.50	0.49	0.45	0.43
	OESW	0.09	0.09	0.09	0.10	0.10	0.085
Na mmol l/l	UCSF	0.66	0.75	0.84	0.84	0.92	1.02
	USCW	0.14	0.14	0.16	0.23	0.23	0.26
	OESF	0.39	0.44	0.49	0.54	0.60	0.62
	OESW	0.04	0.04	0.04	0.06	0.08	0.09
Mg mmol /l	UCSF	0.49	0.54	0.74	0.76	0.80	0.84
	UCSW	0.14	0.15	0.14	0.14	0.15	0.15
	OESF	0.24	0.29	0.30.	0.30	0.33	0.355
	OESW	0.14	0.11	0.15	0.14	0.14	0.15
N %	UCSF	0.31	0.28	0.33	0.30	028	0.32
	UCSW	0.008	0.007	0.01	0.006	0.01	0.008
	OESF	0.28	0.26	0.26	0.30	0.28	0.265
	OESW	0.006	0.007	0.01	0.006	0.01	0.006
P mg/l	UCSF	56.0	68.0	76.0	82.0	87.0	91.0
	UCSW	17.50	18.0	18.0	18.0	20.0	17.0
	OESF	46.0	54.0	60.0	64.0	67.0	72.0
	OESW	11.26	10.88	10.9	11.39	11.26	12.0

Key: *UCSF = Umudike Control Soil (agricultural soil) with fertilizer applied*

OESF = Okigwe Engineering Soil (sub soil) with fertilizer applied

UCSW = Umuahia Control Soil without fertilizer

OESW = Okigwe Engineering Soil without fertilizer

By the above techniques, relationships between the concentration of species in the leachates versus pH of leachant were established, as follows:

Potassium and Calcium

The relationships are described by a linear model of the form:

$$C = \alpha - \beta pH \qquad (1)$$

where α and β are the coefficients (constants)

For N, the applicable equation is of the form

$$C = \alpha \qquad ;(2)$$

where α is a constant and C is independent of pH of leachants.

For Na the relationship is linear and of the form:

$$C = \alpha + \beta\, pH \qquad (3)$$

For phosphate (P), the plot of ($\partial C/ \partial$ pH) vs pH showed a linear decrease, giving rise to the equation:

$$\partial C/\partial \, pH = \alpha - B\, pH \qquad (4)$$

Hence the relationship between C and pH obtained by integrating equation 4 is of the form.

$$C = \alpha\, pH - \beta\, (pH)^2 + k \qquad (5)$$

where α, β and k are the coefficients of the equation, $\beta = {}^1/_2 B$ of equation (4). This is a quadratic relationship, which was also confirmed when the data of Table 4 were fed into a computer-aided quadratic regression programme. The correlation coefficient was 0.996 for P in UCS soil and 0.994 for P in OES soil.

Magnesium (Mg): For Mg, the plot of ($\partial C/ \partial pH$) versus pH showed an exponential decrease which took the form:

$$\ln((\partial C/ \partial pH) = \alpha - \beta\, pH \qquad (6)$$

where α and β are constant

Integration of the above expression gives the equation

$$C = \frac{10^{\alpha}}{2.303\beta} 10^{-(pH)\beta} + k \quad (7)$$

where α, β, and k are constants.

Equation (7) could also be written as:

$$C = k - Q\,10^{-(pH)\beta} \quad (8)$$

where Q, β and k are constants; and

$$Q = (10^{\alpha}/2.303\beta)$$

Either of equations (7) or (8) is described as a modified exponential relationship (Levenbach and Reuter 1976).

The data of Table 4 have been plotted for K, Na and Ca, N and P, and Mg in figures 1,2,3 and 4 respectively. In each case the line of best fit generated by the respective model equations (ie equations 1,2,3,5 and 7) for the elements have also been drawn through the scatter plots.

Figures 1,2,3 and 4 show clearly that the models derived for each element is a satisfactory mathematical representation of the relationship between the quantities (concentration) of the element leached and the pH of the leachant. They also show that the model obtained for each element is identical in form in both soils studied.

The magnitudes of the coefficients α, β, and K of the model equations (equations 1 - 3, 5 and 7) used for deriving the lines of best fit drawn in figures 1 - 4 are tabulated in Table 5.

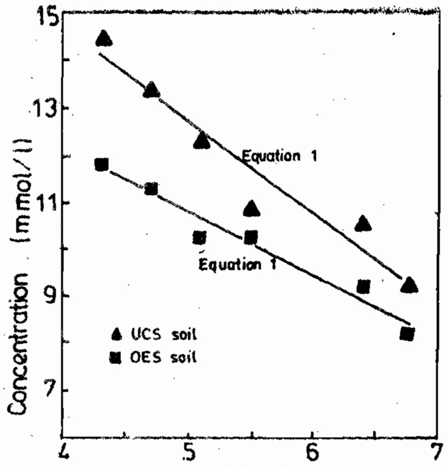

Fig. 1 : Concentration of potassium (K) in leachate versus pH of leachant.

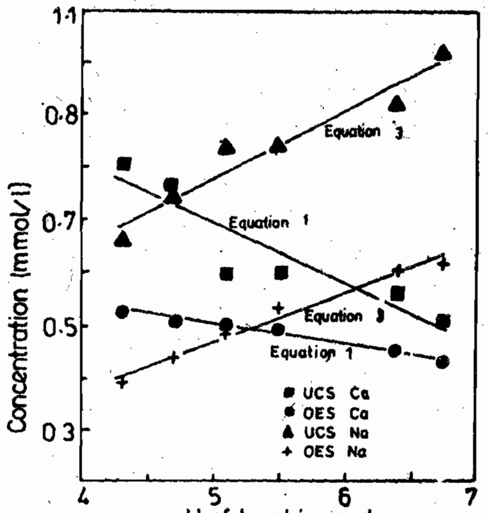

Fig. 2 : Concentration of element (Na+Ca) in leachate versus pH of leachant.

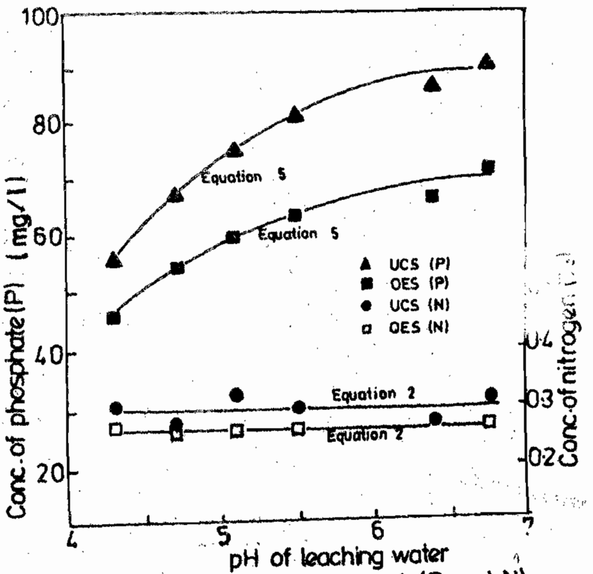

Fig. 3 : Concentration of element (P and N) in leachate versus pH of leachant.

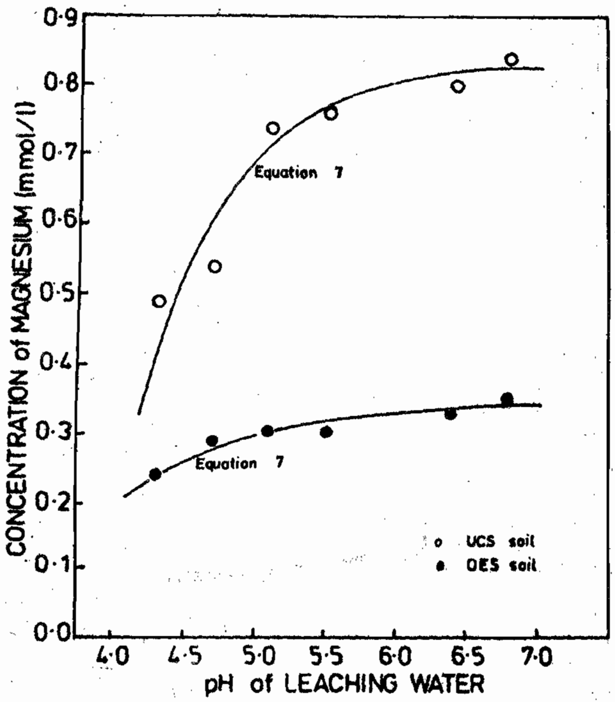

Figure 4 · Concentrations of Magnesium (Mg) in leachate versus pH of leachant.

TABLE 5: MAGNITUDES OF THE COEFFICIENTS A, B AND K EVALUATED FOR MODEL CURVES IN UCS AND OES SOILS

		COEFFICIENTS			APPLICABLE
COMPONENT	SOIL	‖	‖	k	MODEL
K	UCS	22.45	1.95	-	Equation (2)
	OES	17.60	1.35	-	Equation (2)
N	UCS	30.3	0	-	Equation (3)
	OES	27.0	0	-	Equation (3)
P	UCS	80.85	6.10	178.1	Equation (6)
	OES	50.28	3.68	101.7	Equation (6)
Ca	UCS	1.27	.116	-	Equation (2)
	OES	.70	.039	-	Equation (2)
Na	UCS	.145	.127	-	Equation (1)
	OES	.0067	.0928	-	Equation (1)
Mg	UCS	2.82	.694	.83	Equation (11)
	OES	1.28	.502	.348	Equation (11)

Significance of the results

In each leaching experiment conducted above, water containing dissolved CO_2 at a known pH was allowed to pass over solid fertilizer, dissolve its components, and carry them through a given soil sample. The effluent was collected and analyzed to give the data presented and treated above. It follows that the changes in the effluent concentrations of the components as evaluated are expressions of the effects of pH of the leaching water, as distinct from soil pH, on (a) the solubilities and (b) the interactions e.g. ion exchange etc between the components in aqueous solutions and in the particles or micelles of the soil.

Both solubility and the interactions in the soil are thermodynamic or mass action processes. Their equilibria involve the overall concentrations of each of the components contributed to the solution from both the applied fertilizer and the untreated soil. The results of the control experiments show that the contributions to the leach ate concentrations from the soils are negligible compared to the fertilizer. Essentially therefore, neglecting the results from the control experiments does not significantly affect the observations made in this study and the deductions arrived at. Thus, the models derived above for the effects of the pH of leachant water on each of the components of fertilizer are based on valid data.

Also, the infiltration and percolation of rainwater into and through in situ soils with fertilizer follow similar patterns described above involving laminar flow, dissolution of applied fertilizer and interaction of the dissolved components of fertilizer with the soil (Tan, 1975) Although however, there are differences in velocity of flow through soils in both the natural and the artificial cases, it is noteworthy by comparison of data from the two soils that the models obtained in the above experiments are independent of velocity of flow and type of soil.

Thus the model equations obtained above may be reliably applied to the natural case of rainwater passing through applied fertilizer in soils.

An inspection of the data of Table 3 and 6 shows that for the two soils studied and for any fertilizer component investigated, the quantities leached by the same throughput of water at a given pH are always greater for the UCS (clay) soil than the OES (sandy loam) engineering soil. This could be attributed to the greater clay content of the UCS soil. However the leaching rates i.e magnitudes of the component mass flux (McCabe *et al,* 1973) are higher in the OES soil as shown in Table 6, possiblv due to differences in pore sizes between the two soils.

It is noted also that identical models apply for the same component in both soils and that each of the constants α, β, k and Q as applicable to each fertilizer component has a higher magnitude for UCS than for OES. It follows therefore that the coefficients α, β, k and Q obtained for the applicable models for each component are characteristic properties of the soils and could serve as quantitative bases for discriminating between soils and for characterizing them. Obviously, the magnitudes of the constants are influenced by the physicochemical properties of the soils especially ion exchange capacities and soil structure (Tan, 1975).

CONCLUSION

The studies have shown that the dependence of the quantities of the components of applied NPK fertilizer leached in soils on the pH of the input leaching water may be expressed by definite mathematical models.

The leaching of nitrogen (N) is independent of the pH of water. For K and Ca, the equations are linear with negative slopes while for Na the equation is linear with a positive slope. In the case of P, the relationship is quadratic whereas for Mg it has a modified exponential dependence of the form (Levenbach and Reuter, 1976):

$$C_{mg} = k - Q10^{-pH.\beta}$$

where k, Q and β are constants.

Table 6: AVERAGE FERTILIZER COMPONENT FLUX THROUGH COLUMN

($F = C v \times 10^{-3}$ expressed in (mole or mass quantity unit) $m^{-2}h^{-1}$)

	LEACHANT	1	2	3	4	5	6
	pH	4.31	4.78	5.10	5.50	6.40	6.76
COMPONENT	COLUMN						
	IDENTITY						
K	UCSF	0.595	0.551	0.508	0.447	0.434	0.381
Mol l^{-1}	OESF	5.65	5.59	5.08	5.08	4.56	4.08
Ca	UCSF	0.0333	0.317	.0247	0.0247	0.0230	0.208
Mol l^{-1}	OESF	0.261	0.252	.247	0.247	0.222	0.212
Na	UCSF	0.271	0.300	0.300	0.0345	0.0378	0.419
Mol l^{-1}	OESF	0.192	0.217	0.242	0.266	0.296	0.306
Mg	UCSF	0.201	0.0222	0.0304	0.0313	0.0329	0.0345
Mol l^{-1}	OESF	0.118	0.143	.148	0.148	0.163	0.175
N	UCSF	0.0127	0.0115	.0136	0.0123	0.0115	0.0132
%	OESF	0.138	0.128	.128	0.148	0.138	0.131
P	UCSF	2.303	2.80	3.13	3.37	3.58	3.74
Mg/l	OESF	22.70	26.6	29.6	31.6	33.1	35.5

C = component composition in leach ate, v = average fluid velocity through soil (Table 3)

The model equations have been shown to apply almost perfectly for two widely dissimilar South Eastern Nigeria soils. The coefficients of each model equation for the two soils have been evaluated and a comparison of their values in both cases indicates that the coefficients of the model equations are characteristics of each of the soils. It could be concluded from the above that in general, the coefficients (more specifically the β factor) could form a quantitative basis for predicting the effects of variations in the pH of rainwater on the leaching of fertilizer components applied *in situ*.

These concepts could find useful applications in formulations of fertilizer compositions and in the prediction and control of the impacts of rainwater on the substrata and ground waters due to leaching of fertilizer components.

The above findings also emphasize the need to accompany all periodic rainfall data with statements of the values of the pH of the rainwater.

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