

## Determination of Some Anions along the Profile of Irrigated Farm Soils

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**Abstract:** Concentrations of Phosphates ( $\text{PO}_4^{3-}$ ), Nitrates ( $\text{NO}_3^-$ ), Sulphates ( $\text{SO}_4^{2-}$ ), Chlorides ( $\text{Cl}^-$ ), soil pH and organic matter were measured along the profile of irrigated agricultural soils collected in Zaria, a town in Northern Nigeria. The result showed that the irrigated factor, agricultural factor and anthropogenic factor all contributed to the relations between selected chemical properties. The results showed that only chlorides seem to intrinsically relate to the soils.

**Key words:** Anions, profile, soil, irrigated farm, Nigeria

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### INTRODUCTION

Salts of various kinds are found in most soils and many are essential to plant growth. However, some soils contain excessive concentrations of certain salts, which can damage plants. Such soils are referred to as saline soils. High concentrations of such salts as chloride of sodium and boron can be harmful to some plants. Phosphates, nitrates, sulphates, chlorides, soil pH and organic matter have found wide spread use in the evolution of the soil medium for crop growth and need to be in available and sufficient quantities for the best crop yield to be obtained therefore, their concentrations and levels in the soil must be ascertained. The pH of the soil also must be ascertained because the solubility of these ions in the soil and many biological processes in the soil are pH dependent. The organic matter content in the soil must also be determined because it is the main source of energy to soil microbes and without it, biochemical activity in the soil will be practically impossible. Organic matter refers to all vegetable and animal material, which includes the highly decomposed colloidal soil fractions known as humus formed in or added to soils regardless of the stage of decomposition (Allison, 1973; Brady, 1974). Organic matter is responsible for the friable condition of productive soils, an important source of elements such as phosphorus, sulphur and nitrogen (Allison, 1973) and through its effect on physical conditions, increases the water-holding capacity of soils (Kononova, 1975). Most tropical soils have suffered drastic reductions in soil organic matter due to soil erosion and inappropriate land uses (Mbagwu, 1992) thereby making predictions of these ions inconsistent in these soils (Oti, 2002).

Phosphates, nitrates and sulphates are macronutrients, while chlorides are micronutrient. The

total quantity of these ions in the soil is not necessarily a reliable parameter of its availability to the plants (Johnson *et al.*, 1997). Phosphorus (P) is an essential element classified as a macronutrient and, in soils P may exist in many different forms (i.e., solution P, active P and fixed P) (Uzu *et al.*, 1975; Busman *et al.*, 2002) and is considered to be relatively immobile in the soil system (Brady and Weil, 1999) and this immobilization or fixation is related to the presence of aluminum silicates, hydrous oxides of iron and aluminum and alkaline or strongly acidic soil. The amount of phosphorus in irrigated soil horizons below plough layers tend to decrease gradually in magnitude although some deviations from this trend may be observed.

Nitrogen in soils plays a major role among elements necessary for plant growth (Gupta and Chandrashekarhan, 1997) and any nitrogen not adsorbed by plants will be lost by volatilization of ammonia, bacterial denitrification, leaching and chemical reactions of nitrites in soils. Only slight losses occur at pH level between 6 and 7 but quite appreciable losses do occur as pH increases (Russell, 1973). The magnitude of nitrate leaching will depend on the amount of nitrates in the soil, amount and time of rainfall, infiltration and percolation rates and also the water-holding capacity of the soil (Brady, 1974).

Sulphur in soils exists in both organic and inorganic forms. Sulphate is the most important form of inorganic sulphur in soils and is the most readily available form to plants (Alves and Lavorenti, 2004). The fate of sulphate in the soil is influenced by many chemical, biological and physical factors. Therefore, the concentration of sulphate in natural soils can be very variable in both space and time (Schnug and Haneklaus, 1998; Bloem *et al.*, 2001), making it very difficult to assess sulphate availability for

soil fertility management purposes and improved understanding of the dynamics of sulphur in the soil-plant system is an important issue for sustainable production (Cichota *et al.*, 2004). Soil hydraulic properties and ion adsorption are two main soil characteristics affecting sulphate leaching-storage processes in soils (Cichota *et al.*, 2004) and this depends on the pH of the soil, type of clay, clay content and exchangeable cations.

In the soil solution, chlorine occurs predominantly as the Chloride Ion (Cl<sup>-</sup>) and it is an essential micronutrient for higher plants. Natural inputs of chloride to soils come mainly from rainwater, dust and air pollution. In addition, human practices, such as irrigation and fertilization, contribute significantly to chloride deposition. The Cl<sup>-</sup> does not form complexes readily and shows little affinity (or specificity) in its adsorption to soil components. Thus, Cl<sup>-</sup> movement within the soil is largely determined by water flows (White and Broadley, 2001; Öberg and Sandén, 2005).

Modern high intensity agriculture often leads to loss in soil fertility, erosion and can pose long term environmental implications an increase in contaminant emission may have a substantial implication on local agriculture, as heavy metal and other chemical material may enter and even accumulate in agricultural soils through agricultural activities and atmospheric deposition, which could enhance the risk of chemical contamination of the food chains in agricultural ecosystem (Li *et al.*, 2008). Hence, it is important to assess the environmental quality in the farming area. Present study focuses on storage of these ions and their dynamics in two irrigated agricultural soils within River Kubani and River Galma flood plains in Zaria, a town in Northern Nigeria.

**Description of study area and soil sampling:** Irrigated agricultural soils, from two study areas were selected in Zaria, a semi arid region of northern Nigeria. One hundred and twenty soil samples were collected from these sites. Sixty of these were sampled along River Galma and another 60 along River Kubani (a tributary of the Galma River). Much of the study area, which is about 10 ha of farm comprises undulating low, middle and upper slopes. Soils in the study area are mainly sandy-loam in texture. Increasingly the land is being used for intensive purposes such as vegetable and cereal cropping.

Topsoil and subsoil were sampled separately. The surface dirt was scraped away and then samples collected from the 0-5 cm depth and separate samples from the 5-60 cm depth using a steel auger to bore the soil. The areas sampled were limited to a uniform soil type or

condition within the farming area. Separate samples were collected from where, the slope of the land changes substantially and close the river banks. Sample locations are selected at random, with equal probabilities of selection and independently from each other. The rationale is to exclude any form of bias, such as a conscious or even unconscious process of discriminatory selection on parts of the individuals. The samples were air-dried for 2 weeks before composting at room temperature (32°C) with subsequent storage in sealed polyethylene containers (Ma *et al.*, 2005). Thirty composite samples were made for the two sampling locations and the area included in one composite sample was about 1.2 h. Composite soil samples were manually homogenized, ground manually and passed through 200 µm sieve. Samples were coded K for Kubani area and G for Galma area. Samples collected along the slope were coded S and those on plain were coded P and samples collected close to the river bank was coded B. Three locations, where intensive farming took place were sampled in both Kubani and Galma areas and coded 1-3. All soils were collected between February and March 2006.

## MATERIALS AND METHODS

**Soil pH:** It was measured by standard procedures, using a 1:5 soil to water suspension (pH<sub>w</sub>).

**Determination of organic matter:** The loss on ignition method was used. The quantitative ashing of soil samples at 450°C gave an estimate of the organic matter content in the soil. Organic carbon can also be estimated by this method by multiplying the results obtained by 0.58.

**Extraction of Anions:** Hydrochloric acid (0.01 mol DM<sup>-3</sup>) was used to extract phosphates, while distilled water was used to extract sulphates, nitrates and chlorides. A 0.5 g of the soil samples were transferred into conical flasks (75 cm<sup>3</sup>) containing of hydrochloric acid (20 cm<sup>3</sup>) or distilled water (20 cm<sup>3</sup>) as the case may be and transferred to a mechanical shaker for 20 min. The samples were then filtered using No. 42 Whitman filter paper. Suitable aliquot were then transferred into 50 cm<sup>3</sup> volumetric flasks for further analysis.

**Determination of nitrate:** The Kjeldahl method was used for the analysis of nitrate-N (Agbenin, 1995).

**Determination of phosphate:** The molybdenum blue method was used for the analysis of phosphate-P (Agbenin, 1995).

**Determination of sulphate:** Turbidimetric method was used. The method is based on the estimation of the turbidity produced when sulphate ions react with barium chloride and the turbidity was measured as absorbance (Allen *et al.*, 1974).

**Determination of chloride:** Mohr's Method was used. This method is a titrimetric technique based on the fractional precipitation of silver chloride (AgCl) by silver nitrate (Allen *et al.*, 1974).

### RESULTS AND DISCUSSION

The soils in the sampled areas along the Kubani River are generally sandy loam in texture, slightly acidic and relatively high in organic matter content except samples collected along the slope (KS), where little or no farming activity took place (Table 1a-e). Generally, the organic matter decreased along the soil profile, however, KB and KP3 decreased only slightly with relatively low coefficient of variation. The soils in farms along the Galma River have relatively higher clay content compared to Kubani and are relatively more acidic. The result obtained for organic matter content in the soil along the Galma River were generally lower compared to those obtained for soil samples collected along the Kubani river (Table 2a-e). In most cases, the organic matter content decreased along the soil profile with sporadic increases at some points. This increases also showed increases in the phosphate concentrations at this points in the profile. It was also observed that the organic matter content of the soils in this sampling area have relatively higher coefficient of variation compared to those along the Kubani river. Like the samples along the river bank of the Kubani, GB samples showed relatively high organic matter compared to other locations at similar depth. pH is an important attribute of soils because it affects the solubilities of the various ionic species, the bonding of the ions to exchange sites and microbial activity in the soil (Brady, 1974). In moderately neutral to strongly acidic soils for instance, phosphates becomes less available through interactions with Fe (OH)<sub>3</sub> and Al (OH)<sub>3</sub>. At high pH, phosphates become increasingly insoluble because of their interactions with Ca<sup>2+</sup> to form apatite and other precipitates (Brady, 1974). The pH values for samples along the Kubani are fairly constant along the soil profile with very small coefficient of variance, except for samples collected close to the river bank (KS) that showed increasing acidity down the profile. The pH of the Galma soils generally decreased along the soil profile with very small coefficient of variation.

Table 1a-e: Concentration of the ions showing the mean, maximum and minimum values for soil profiles in sampled areas of Kubani

Statistical values	Phosphates	Sulphates	Nitrates	Chlorides	pH	Org. matter
<b>a) KP1</b>						
Mean	53.0800	11.050	7.780	57.63	6.2600	29.300
Max.	99.1700	18.900	17.000	97.52	6.3800	49.420
Min.	4.7500	8.100	0.300	35.46	6.2100	8.510
C.V	4.9900	0.260	0.970	1.70	0.0001	1.710
<b>b) KP2</b>						
Mean	55.1200	16.300	23.170	76.83	6.6300	26.720
Max.	223.2500	21.600	45.000	70.92	6.7200	88.740
Min.	2.2000	8.100	5.000	68.65	6.5400	4.870
C.V	22.7900	0.240	1.360	0.11	0.0001	6.790
<b>c) KP3</b>						
Mean	133.6600	11.070	12.320	62.06	6.210	54.800
Max.	187.3200	20.400	19.000	79.79	6.310	76.460
Min.	86.4000	6.800	0.600	44.33	6.060	38.340
C.V	1.7700	0.410	0.660	0.51	0.003	0.680
<b>d) KB</b>						
Mean	135.6600	11.270	5.780	54.67	5.9800	57.020
Max.	153.3000	16.020	7.000	70.92	6.3200	64.660
Min.	110.8800	5.400	4.500	44.59	5.6300	46.770
C.V	0.3000	0.265	0.024	0.42	0.0023	0.114
<b>e) KS</b>						
Mean	6.7900	13.780	6.500	63.51	6.140	5.050
Max.	20.1600	20.400	11.200	97.56	6.340	13.030
Min.	2.1000	10.800	3.000	35.46	5.940	1.640
C.V	1.2027	0.160	0.250	1.60	0.007	0.660

Table 2a-e: Concentration of the ions showing the mean, maximum and minimum values for soil profiles in sampled areas of Galma

Statistical values	Phosphates	Sulphates	Nitrates	Chlorides	pH	Org. matter
<b>a) GP1</b>						
Mean	23.25	16.120	8.3300	81.2700	5.9300	22.52
Max.	75.52	20.800	12.0000	124.1100	6.4100	36.85
Min.	1.60	10.800	6.0000	43.3300	5.4800	1.29
C.V	6.10	0.220	0.0100	1.9000	0.0044	2.56
<b>b) GP2</b>						
Mean	26.43	10.180	6.5500	84.2200	6.6200	2.47
Max.	76.80	20.400	13.0000	132.9800	6.7800	34.39
Min.	1.60	2.700	3.1000	53.1900	6.4500	1.81
C.V	8.98	0.840	0.3200	2.0400	0.0005	3.52
<b>c) GP3</b>						
Mean	42.88	5.180	9.6700	35.4600	5.9900	19.43
Max.	126.72	13.500	22.0000	44.3300	6.5100	54.65
Min.	1.60	1.350	0.8000	26.6000	4.8400	1.39
C.V	10.77	0.690	1.7900	1.4800	0.0130	4.24
<b>d) GB</b>						
Mean	118.24	4.740	6.2100	50.2900	5.3900	50.79
Max.	142.72	12.200	10.9000	62.0600	5.6400	61.98
Min.	59.20	1.350	0.8400	35.4600	4.8900	26.28
C.V	1.33	0.680	0.4800	0.3825	0.0026	0.54
<b>e) GS</b>						
Mean	11.25	6.0000	5.7400	79.7900	5.6900	6.57
Max.	53.76	17.7000	9.5000	115.2500	6.0600	26.75
Min.	1.60	1.3500	3.1000	53.1900	5.2000	1.82
C.V	6.44	1.1747	0.0013	1.7700	0.0040	2.50

Phosphorus (P) is an essential element classified as a macronutrient because of the relatively large amounts of P required by plants. Phosphorus is one of the three nutrients generally added to soils in fertilizers. Results for phosphate showed concentrations >150 mg/100 g surface soils (0-5 cm) for KP2, KP3 and KB soil samples. These

areas correspond to the areas that received the highest measure of fertilizer. The phosphate concentration decreased along the soil profiles. KP2 decreased faster with the highest coefficient of variation, while the KB had the least. Phosphate concentrations are generally lower than those obtained for the Kubani samples, with coefficient of variation fairly constant except for GB samples, where it is 1.3. The GB showed some similarity with the KB samples, by being the least variable along the profile. A very strong correlation was found between the phosphate concentration and the amount of organic matter down the profiles of all the areas sampled in the Kubani and the Galma areas (in all cases  $r$  was not  $<0.99$  at  $p>0.1$ ).

Nitrate concentration in soil profiles did not show a clear trend. The concentrations obtained were low for KB, KP1, KS samples, not exceeding 6.2 mg/100 g in the surface soils and some cases below detection level at some points along the soil profile. Unlike phosphate, nitrate did not show any correlation with organic matter. Nitrate concentrations in the Galma area were generally  $>3.0$  mg/100 g in the entire surface soils. Like those of the Kubani River, there is not clear cut trend along the soil profiles of the Galma soils, however, lowest concentrations were observed at bottom profiles of GB and GP3 soil samples.

Sulphur, as one of the essential macronutrients to plants, has never received the same attention as other nutrients like nitrogen, phosphorous and potassium, although sulphur is required in similar amounts as phosphorous and magnesium (Abbasi *et al.*, 1987). Sulphur is one of the most important nutrients for plants. Its deficiency can cause yield losses and retention of sulphate in soils is highly dependent on pH and mineralogy and some studies have shown that the accompanying cation can also be important (Cichota *et al.*, 2004). Sulphate is the most important form of inorganic sulphur in soils and is the most readily available form to plants because sulphates are resistant to leaching. The fate of sulphate in the soil is influenced by many chemical, biological and physical factors and the ability of the soil to adsorb the sulphates occurs above a pH of 6.5 but adsorption increases as pH decreases (Cichota *et al.*, 2004), this was not observed in this study. Fluctuations in the amount of soluble sulphates in the soil profile may occur as a result of leaching, mineralization of organic sulphur and uptake by plants. Concentrations of sulphates were the lowest of the four ions investigated along the Kubani. The trends along the soil profiles were not too clear especially in areas, where farming took place (KP1-KP3). The coefficients of variations along the profiles were relatively small especially for KS samples.

Sulphate decreased along the soil profiles of the sampled areas of the Galma river. The surface soils are richer in sulphate and it is only in the GP1 samples that the concentration did not go below 10 mg/100 g.

The Cl content of the soil is not an intrinsic property of the soil, but is a result of soil management, because of its mobility in the soil and the fact that it moves with the water in the soil. The Cl ion is not adsorbed on soil particles at neutral and alkaline pH values and therefore is easily leached (Fixen *et al.*, 1987). The concentrations of chlorides are especially high in the surface soils and in all cases higher than the concentrations of nitrates and sulphates. The concentration of the ion in KP2 was fairly constant along the profile, showed some decrease along the profile for KB and KS samples. The chlorides concentrations in the Galma area are in some cases are higher than those obtained along the Kubani River. The variation long the profiles are relatively low with the highest being the GP2 with a coefficient of variation 2.04.

Correlation coefficient and student's t-test were performed to compare and see whether there is any similarity on how these ions vary in the soil profiles of both farms. Only results that were found to be significant are presented in Table 3. In some cases, such as the variation of sulphate in KP1/GP1 pair, the pattern of variation were significantly correlated ( $r = 0.623$ ), while the t-test gave non significant result (0.023). This means that the pattern of variation was similar, but the pattern was in both cases not similar. Among the ions studied, phosphate in both farms show the highest level of correlation, while in all cases the way these ions vary was not similar. This shows that in both farms, each of the anion show different pattern in the way they vary. This may be as a result of the slightly different soil types in the farms, quality of water, type of farming practice and management and the frequency of irrigation in both farming areas.

Table 3: Comparing the behaviour of ions in sampled locations of Kubani and Galma farming areas; results of Student's t test and Pearson correlation

Samples	Ion	Correlation coefficient (r)	Student's t-test
KS/GS	PO <sub>4</sub>	0.945	0.482
KB/GB	-	0.924	0.061
KP1/GB1	-	0.683	0.059
KP2/GB2	-	0.850	0.281
KP3/GB3	-	0.883	0.000
KP1/GP1	SO <sub>4</sub>	0.623	0.023
KS/GS	NO <sub>3</sub>	0.870	0.304
KB/GB	-	0.550	0.796
KP1/GP1	-	0.653	0.817
KP2/GP2	-	0.732	0.057
KP3/GP3	-	0.357	0.668
KB/GB	Cl	0.787	0.203
KP1/GB1	-	0.649	0.297
KP2/GB2	-	0.203	0.620
KP3/GB3	-	0.612	0.002

## CONCLUSION

The pH values of the top soils are generally >6.0 and did not correlate with the concentrations of the anions. The results showed that the concentration of phosphates correlates with organic matter in the soils of these irrigated farmlands. The concentrations of sulphates down the profiles did not show a clear trend but the mobilization seem to be dependent amount of water supply, infiltration rates, percolations rates and water holding capacity of the soils. Nitrate concentrations also did not show a clear trend, which may be as result of losses due to denitrification. The concentration of chlorides varied very little in all the soil samples but show a general decrease down each soil profile. These ions are usually inputs from the most anthropogenic sources, related and not related to agricultural practices, of general and local or incidental concern. These sources include those from commercial fertilizers, agrochemicals, sewage sludges and other wastes used as soil amendments, irrigation waters and atmospheric depositions from urban and other sources.

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