Effect of Phosphate levels on vegetables irrigated with wastewater

S O Oladeji¹ and M D Saeed²

¹Polymer Technology Department, Hussaini Adamu Fed. Polytechnic, Kazaure, Jigawa State, Nigeria
²Chemistry Department, Bayero University Kano, Kano State, Nigeria

E-mail: saheedilori75@gmail.com

Abstract: This study examined accumulation of phosphate ions in wastewater and vegetables through man-made activities. Phosphate level was determined in wastewater and vegetables collected on seasonal basis along Kubanni stream in Zaria using UV/Visible and Smart Spectro Spectrophotometers for their analyses. Results obtained show that phosphate concentrations ranged from 3.85 – 42.33 mg/L in the first year and 15.60 – 72.80 mg/L in the second year for wastewater whereas the vegetable had levels of 3.80 – 23.65 mg/kg in the year I and 7.48 – 27.15 mg/kg in the year II. Further statistical tests indicated no significant difference in phosphate levels across the locations and seasons for wastewater and vegetables evaluated. Correlation results for these two years indicated negative (r = -0.062) relationship for wastewater while low (r = 0.339) relationship noticed for vegetables planted in year I to that of year II. Phosphate concentrations obtained in this study was higher than Maximum Contaminant Levels set by Standard Organization such as WHO and FAO for wastewater whereas vegetables of the sampling sites were not contaminated with phosphate ions. Irrigating farmland with untreated wastewater has negative consequence on the crops grown with it.

1. Introduction
Phosphorus is a naturally occurring element in the environment that can be found in all living organisms as well as in water and soils. It is an essential component for many physiological processes related to proper energy utilization in both plants and animals [1]. It normally occurs in nature as part of a phosphate ion (PO₄³⁻), consisting of a phosphorus atom and 4 oxygen atoms; the most abundant form is orthophosphate. On land, most phosphate is found in rocks and minerals. It can be added to the environment by man’s activities as point source discharges or as non-point source runoff. Typical sources include industrial and municipal wastewater discharges or runoff from agricultural lands or urban areas. Livestock derive part of their phosphate needs from plant materials. However, much of the naturally occurring phosphate in grains is in an indigestible form [2]. Therefore, inorganic phosphates sources are added to poultry and swine feeds to ensure adequate nutrition and to prevent rickets. As a result, much of the dietary phosphate passes through livestock and poultry and is excreted in animal manure. Utilizing animal manure as a fertilizer on crop and grazing land can recycle nutrients. Plants uptake phosphate from soil mostly in the orthophosphate forms. Natural soil phosphate level is often low enough to limit crop production. Both inorganic phosphate fertilizers (treated rock phosphate) and organic phosphate sources (animal manures) are equally adept at supplying the orthophosphate ion and correcting phosphate deficiencies in soil [3]. Most of the
phosphates in animal manure are in an organic form and must be converted to plant-available forms via soil biological activity, a process known as mineralization. The net effect of this characteristic is that phosphate derived from animal manure act more like a slow-release fertilizer than commercial inorganic fertilizers, which are more soluble and readily available to plants [4].

Phosphorus is an essential nutrient for plants and animals. It is a limiting nutrient for aquatic organisms. Phosphorus forms parts of important life-sustaining molecules that are very common in the biosphere. It does not enter the atmosphere, mostly remaining on land, in rock and soil minerals [5]. Eighty percent of the mined phosphorus is used to make fertilizers. Phosphates from fertilizers, sewage and detergents can cause pollution in lakes and streams [6]. Over enrichment of phosphate in both fresh and onshore marine waters can lead to massive algae bloom which, when they die and decay leading to eutrophication of fresh water. Phosphates rich deposits have generally formed in the ocean or from guano, and over time, geologic processes bring ocean sediments to land. This study examined phosphate accumulation in wastewater and vegetables of sampling area through man-made activities.

2. Materials and Methods
2.1. Sampling
Sampling was done in three seasons (harmattan, dry and rainy) for two years making six (6) samples per site and this was done using composite sampling technique at point of inlet into the river at five different points along Kubanni stream channels in Zaria, Kaduna State, Nigeria. Sample bottles used were firstly rinsed with sampled water three times before filling to the brim at a depth of one meter below the wastewater from each of the five designated sampling points. These sample bottles were labelled accordingly, stored in ice-blocked coolers and transported to the laboratory while in the laboratory; they were stored in the refrigerator maintained at 4 °C prior to the analysis [7]. Vegetable samples of spinach, lettuce, cabbage, carrot, okra, onion and tomato were randomly handpicked from different garden plots along Kubanni stream channels using hand-gloves, bulked together to form a composite sample, wrapped in envelopes and labelled accordingly. Each vegetable samples were washed with tap water, followed by deionized water, air dried in the laboratory, grounded to powder and sieved using 250 µm sieve [8].

2.2. Phosphate determination in wastewater
100 cm$^3$ of wastewater sample was dispensed inside conical flask; one drop of phenolphthalein indicator was added and thoroughly shaked. The sample turned pink and a few drops of strong acids (HNO$_3$) were added until the pink colour disappeared. The volume of the solution was adjusted to 1000 cm$^3$ with deionized water. To this solution, 4 cm$^3$ of molybdate reagent and ten drops of SnCl$_2$.2H$_2$O solution were added and thoroughly mixed for colour development at the temperature of 30 °C. The solution changed to blue colour, it was allowed to stand for twelve minute and the intensity of colour was measured at 690 nm using JENA Model UV/Visible Spectrophotometer. The blank was prepared by taking 40 cm$^3$ deionized water through the same procedure as in the wastewater sample [7]. Orthophosphate ion combines with ammonium molybdate under acidic condition to form a yellow complex compound known as ammonium phosphor-molybdate. It was then reduced by tin(II)chloride solution in glycerol, the yellow complex is reduced to a blue-coloured compound due to molybdenum blue.

$$\text{PO}_4^{3-} + 12\text{(NH}_4\text{)}_2\text{MoO}_4 + 24\text{H}^+ \rightarrow 4\text{(NH}_4\text{)}_2\text{PO}_4\cdot3\text{MoO}_3 + 12\text{NH}_4^+ + 12\text{H}_2\text{O} \ (1)$$

(yellow complex compound)

$$4\text{(NH}_4\text{)}_2\text{PO}_4\cdot3\text{MoO}_3 + \text{Sn}^{2+} \rightarrow \text{Molybdenum blue} + \text{Sn}^{4+} \ (2)$$
2.3. **Phosphate determination in vegetable samples**

Each of the vegetable samples was chopped into small pieces. The chopped samples were then air-dried. The air-dried samples were ground and sieved with a sieve of 1 mm mesh. Then, 1 g of each of the sieved samples was weighed into acid-washed porcelain crucibles and analyzed as described by [9] using Smart Spectro Spectrophotometer 2000. The results of phosphate in wastewater and vegetables were expressed as bar-charts using Microsoft Excel, these results were subjected to one way Analysis of Variances (ANOVA) and Pearson Product Moment Correlations (PPMC) using Statistical Package for the Social Sciences (SPSS) 20.0 version software.

### 3. Results and Discussion

![Figure 1. Concentrations of phosphate in wastewater across seasons.](image1)

![Figure 2. Concentrations of phosphate in vegetables analyzed.](image2)
Figure 1 show phosphate concentrations in wastewater from Kubanni stream channels. The concentrations determined were in the range of 46.07 – 143.20 mg/L for the first year. Highest level of 143.20 mg/L was obtained at Sabon-gari during the rainy season followed by 130.70 mg/L at the same season but in Unguwa-fulani and this was closely followed by 128.20 mg/L at the same Unguwa-fulani but in the harmattan season while the least concentration of 46.07 mg/L was recorded at Industrial area along Jos road in the rainy season. Elevated levels of phosphate during harmattan and rainy seasons could be as a result of runoff from agricultural land, sewage and detergents as suggested by [3]. Phosphate levels were also high at these sampling sites; Kwangila (123.54 mg/L) in the rainy season, Tundun-wada (123.20 mg/L) during the harmattan season and Sabon-gari (110.74 mg/L) in the harmattan season. Phosphate concentrations were generally high in wastewater for year I which might be due to heavy discharged of effluents from municipal and industrial areas as suggested by [10]. The concentrations determined were in the range of 5.14 – 22.50 mg/L, in second year. Highest concentration (22.50 mg/L) was recorded at Unguwa-fulani during the harmattan season followed by 20.74 mg/L from the same site but in the dry season while the lowest level of 5.14 mg/L was noted at Kwangila sampling site during the rainy season. The chart showed low levels of phosphate in year II which could be attributed to flooding of first year that led to heavy erosion and washed away most of the phosphates in wastewater as suggested by [2]. Other sites with low levels of phosphate were; Kwangila (15.04 mg/L), uniform concentrations of 14.08 mg/L were recorded at both Industrial area along Jos road and Sabon-gari while 13.71 mg/L was observed at Tundun-wada, all these results were obtained in the dry season. Comparing the results obtained in year I with that of year II, it was revealed that harmattan season of first year (74.98 – 128.20 mg/L) had high concentration of phosphate in wastewater than harmattan season of second year (5.74 – 22.50 mg/L), likewise, dry season of year I (60.24 – 88.75 mg/L) showed high level of phosphate than dry season of year II (13.71 – 20.74 mg/L). In the same way, rainy season of year I (46.07 – 143.20 mg/L) had high level of phosphate in wastewater than corresponding rainy season of year II (5.14 – 9.24 mg/L). WHO recommends 5 mg/L as maximum contaminant level for phosphate in wastewater before it could be discharged on river and this in indicates wastewaters analyzed are polluted with phosphate ions. [10] reported 103.23 – 164.22 mg/L as phosphate levels in wastewater which was above concentrations obtained in second year while similar to levels obtained in the year one of this study.

Figure 2 presents phosphate levels in vegetables collected along Kubanni stream channels. Determined concentrations ranged from 0.11 – 2.85 mg/Kg for the year one. Highest levels of 2.85 mg/Kg was obtained in spinach planted during the dry season followed by the same spinach (2.20 mg/Kg) in the harmattan season while the least concentration of 0.11 mg/Kg was observed in carrot cultivated during the harmattan season. Spinach showed high level of phosphate than other vegetables analyzed which could be due to its large surface area as suggested by [11]. Other vegetables with low levels of phosphate were; onion (1.72 mg/Kg) planted in the dry season, okra (1.45 mg/Kg) cultivated during the harmattan season and tomato (1.20 mg/Kg) planted in the dry season. Vegetables analyzed had low levels of phosphate in year I, this could be attributed to less solubility of phosphate in water and inability of it to be converted to orthophosphate form that are needed by vegetables despite heavy application of fertilizers as suggested by [12] and [13]. In second year, vegetables studied had concentrations of 0.23 – 8.60 mg/Kg. Highest level of 8.60 mg/Kg was noted in carrot planted in the rainy season followed by spinach (7.50 mg/Kg and 7.48 mg/Kg) both in the dry and rainy season while the least concentration was recorded in okra (0.23 mg/Kg) cultivated in the harmattan season. Dry season of year II showed peak level of phosphate which might be related to heavy application of phosphate enrich fertilizers coupled with the nature of wastewater use for irrigation as stated by [14]. Other vegetables with low levels of phosphate were; lettuce (5.40 mg/Kg) cultivated in the rainy season, tomato (4.14 mg/Kg) planted during the harmattan season and cabbage with level of 3.76 mg/Kg. The chart indicates high level of phosphate in year II than year I which might be related to flooding experienced in year I, this necessitated heavy application of phosphate enriched fertilizer and other chemicals than usual in the following year as observed by [10]. Comparing these years results, it was revealed that harmattan season of year I (0.11 – 2.20 mg/Kg) showed low level of phosphate ions than harmattan season of year II (0.23 – 4.83 mg/Kg). Likewise, dry season of first year (0.37 – 2.85
mg/Kg) had less concentration of phosphate ions than dry season of second year (1.57 – 7.48 mg/Kg). In the same way, rainy season of year I (0.20 – 2.00 mg/Kg) had low level of phosphate ions than corresponding rainy season of year II (0.50 – 8.60 mg/Kg). The phosphate levels analyzed were below the concentrations obtained by other workers including [15] (967.69 – 3390.50 mg/Kg), [10] (32 – 73 mg/Kg) and [6] (33.27 – 187.95 mg/Kg).

Table I presents ANOVA for phosphate levels in wastewater between year one and two. Statistical analysis shows that p = 0.876 > 0.050 this means that there is no significant difference in phosphate levels across the sampling locations as observed from their mean. Phosphate concentrations were also examined across the seasons to establish their differences which indicates p = 0.975 > 0.050 meaning no significant difference across the seasons. This might be as a result of sampling sites are falling within the same vicinity thereby their source of contaminations with phosphate are similar irrespective of change in seasons as observed by [14]. The same table shows p = 0.197 > 0.050 this means that there is no significant difference in phosphate levels among various vegetables analyzed and their mean and standard deviation illustrate this finding. The table also shows p = 0.952 > 0.050 meaning no significant difference in phosphate concentrations across the seasons for vegetables evaluated. PPMC conducted to establish the relationship between phosphate levels between years one to two for wastewater as presented in Table 2. Statistical data showed the mean with standard deviation level for phosphate ion to be 95.661±30.993 in year I while 11.955±5.135 was obtained in year II with the Pearson correlation (r) = -0.062, degree of freedom (df) = 13 and p = 0.827 > 0.050 meaning negative relationship. The same table shows low relationship for phosphate levels in vegetables as their data indicates 0.810±0.794 for year I and 3.103±2.501 for year II.

Table 1. ANOVA Results for phosphate in wastewater and vegetables.

| Analysis of Variances          | Sum of Squares | df  | Mean Square | F    | Sig. |
|--------------------------------|----------------|-----|-------------|------|------|
| Phosphate in Wastewater (Locations) | 3021.049        | 4   | 755.262     | 0.298| 0.876|
| Between Groups Within Groups Total | 63345.869       | 25  | 2533.835    |      |      |
|                               | 66366.918       | 29  |             | 2533.835 |      |
| Phosphate in Wastewater (Seasons) | 2148.175        | 5   | 429.635     | 0.161| 0.975|
| Between Groups Within Groups Total | 64218.743       | 24  | 2675.781    |      |      |
|                               | 66366.918       | 29  |             | 2675.781 |      |
| Phosphate in Vegetable (Among vegetables) | 40.6000         | 6   | 6.767       | 1.532| 0.197|
| Between Groups Within Groups Total | 150.146         | 34  | 4.416       |      |      |
|                               | 190.746         | 40  |             | 4.416 |      |
| Phosphate in Vegetable (Seasons) (Groups) | 5.771           | 5   | 1.154       | 0.218| 0.952|
| Between Groups Within         | 184.975         | 35  | 5.285       |      |      |
| Phosphate in Vegetable Total (Groups) | 190.746         | 40  |             | 5.285 |      |
### Table 2. PPMC Summary for phosphate in wastewater and vegetables.

| Variables           | \(N\) | \(\overline{x}\) | SD | \(r\)  | df | Sig. |
|---------------------|-------|-------------------|----|--------|----|------|
| Phosphate Year I    | 15    | 95.661            | 30.993 | -0.062 | 13 | 0.827 |
| Phosphate Year II   | 15    | 11.955            | 5.135  |        |    |      |
| Phosphate Year I    | 21    | 0.810             | 0.794  | 0.339  | 19 | 0.133 |
| Phosphate Year II   | 21    | 3.103             | 2.501  |        |    |      |

### 4. Conclusion

Contamination of the stream with phosphate affects the vegetables that are irrigated with the water. This may interfere with food chain and affect the human consumers of these vegetables. The study showed that wastewater and vegetables across the locations and seasons indicated no significant difference in the samples analyzed which majorly due to anthropogenic activities. Periodical monitoring of anion levels along the stream should put in place as to evaluate their environmental impacts in order to assess their possible potential risks.

### References

[1] Hu H 2002 Human Health and Heavy Metals Exposure, In: Life Support: The Environment and Human Health ed M McCally (London: MIT Press) p 134 – 140

[2] Ademoroti CMA 1996 Standard Method for Water and Effluents Analysis (Ibadan: Foludex Press) p 22 – 112

[3] Edward GP, Molof AH and Schneeman P 1990 JAWWA Determination of orthophosphate in fresh and saline water 57 917 – 21

[4] Williams CH and David DJ 1973 Australian J. Resource 11 43 – 56

[5] Alloway BJ and Ayres DC 1993 Chemical Principles of Environmental Pollution ed Blackie (London: Chapman and Hall) p 190 – 242

[6] Akan JC, Abdulrahman FI, Sodipo OA and Lange AG 2010 J Amer. Sci. 6 78 – 87

[7] Arnold E and Mary AH 1998 Standard Methods for the Examination of Water and Wastewater (Washington DC: APHA Press) p 45 – 60

[8] Munson RD and Nelson WL 1990 Principle and Practices in Plants Analysis in “Soil Testing and Plant Analysis (ed) RL Westerman (London: Mandison) p 359 – 87

[9] Radojevic M and Bashkin VN 1999 Practical Environmental Analysis (Cambridge: Royal Society of Chemistry Press) p 466 – 75

[10] Akan JC, Abdulrahman FI, Dimari GA and Ogugbuaja VO 2008 Euro. J. Sci. Res. 23 122 – 33

[11] Cantliffe DJ 1973 Agro J 65 563 – 65

[12] Razzaque MS 2009 Amer. J. Physio. & Renal Physio. 296 470 – 76

[13] Singh BR 1994 Environmental Rev 12 133 – 46

[14] Oladeji SO 2017 Archives of Agri. and Env. Sci. 2(3): 141 - 47

[15] Uwah EI, Akan JC, Moses EA, Abah J and Ogugbuaja VO 2007 Agri. J. 2: 392 – 9

[16] Farooq M, Anwar F and Rashid U 2008 Pak. J. Botany 40: 2099 – 106