Australian Journal of Basic and Applied Sciences, 4(5): 779-784, 2010
ISSN 1991-8178

# Fluoride Content of Soil and Vegetables from Irrigation Farms on the Bank of River Galma, Zaria, Nigeria

Okibe F.G, Ekanem E.J, Paul E.D, Shallangwa G.A, Ekwumemgbo P.A, Sallau M.S, Abanka O.C.

Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria.

**Abstract:** Fluoride content of the soils and some vegetables from three farms near the bank of river Galma, Zaria, Nigeria were estimated by Alizarin red spectrometric method. The mean soil leachable fluoride for all the soils was in the 0.075 - 0.200 mg $Kg^{-1}$ range. At 95 % confidence limit (*p=0.05*), the mean concentration of soil leachable fluoride for soils from the farms A, B, and C investigated were 0.139 ± 0.030, 0.115 ± 0.041, and 0.080 ± 0.005 mg $Kg^{-1}$ respectively. The mean fluoride content in vegetable at the same confidence limit was Cabbage: 0.054 ± 0.0093 mg $Kg^{-1}$, Carrot: 0.035 ± 0.01mg $Kg^{-1}$, and Lettuce: 0.096 ± 0.0199 mg $Kg^{-1}$. The $t_{exp}$ evaluated to compare the averages of fluoride levels in the vegetables using t-test at 95% confidence level (*p=0.05*) for 18 degrees of freedom, 2.10 critical value, were 1.62, 5.77, and 1.84 for lettuce and cabbage, carrot and cabbage, and carrot and lettuce respectively. Significant difference only exists in the fluoride levels of carrot and cabbage with $t_{exp}>$ the critical value. All the values obtained were well below the toxic limit of 2.57-16.44 mg $Kg^{-1}$ in soil and maximum contaminant level of 4.0 mg $Kg^{-1}$ in food and vegetable stipulated by EPA, FAO, and WHO Joint Standard limit for fluoride. The implication of the results is that the use of the Galma river water for irrigation, and the contribution of fluoride to the soil and vegetables from anthropogenic sources within and around the Galma river area, has no deleterious effect on the soil and some vegetables cultivated in farms at the river bank.

**Key words:** Fluoride; Irrigation farm; soil; vegetable; River Galma

## INTRODUCTION

Fluorides are released into the environment naturally through the weathering of minerals, in emissions from volcanoes and in marine aerosols Symonds *et al.,* (1988). The main natural source of inorganic fluorides in soil is the parent rock (WHO, 1984). During weathering, some fluoride minerals (e.g., cryolite or $Na_3AlF_6$) are rapidly broken down, especially under acidic conditions Fuge and Andrews, (1988). Other minerals, such as fluorapatite ($Ca_5(PO_4)_3F$) and calcium fluoride, are dissolved more slowly (Kabata-Pendias and Pendias, 1984). The mineral fluorophlogopite (mica; $KMg_3$ ($AlSi_3O_{10}$) $F_2$) is stable in alkaline and calcareous soils (Elrashidi and Lindsay, 1986)]. However, its solubility is affected by pH and the activities of silicic acid ($H_4SiO_4$) and aluminium ($Al^{3+}$), potassium ($K^+$) and magnesium ($Mg^{2+}$) ions.

Anthropogenic sources of fluoride into the environment include the following: the industrial production and use of chemicals such as, Hydrogen fluoride (HF), Calcium fluoride ($CaF_2$), Sodium fluoride (NaF), Fluorosilicic acid ($H_2SiF_6$), Sodium hexafluorosilicate ($Na_2SiF_6$), Sulfur hexafluoride ($SF_6$), and Phosphate fertilizers (Weas, 1986). Phosphate fertilizers are the major source of fluoride contamination of agricultural soils. They are manufactured from rock phosphates, which generally contain around 3.5% fluorine (Hart *et al.,* 1934). However, during the manufacture of phosphate fertilizers, part of the fluoride is lost into the atmosphere during the acidulation process, and the concentration of fluoride in the final fertilizer is lowered further through dilution with sulphur (superphosphates) or ammonium ion (ammoniated phosphates); the final product commonly contains between 1.3 and 3.0% fluorine (McLaughlin *et al.,* 1996).

Available quantitative information concerning the release of fluoride into the environment (air, water and soil) from industrial sources is limited. Fluoride is released into the environment via exhaust fumes, process

**Corresponding Author:** Okibe F.G, Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria.
Tel: +2347039502969, +2348029351361
Email: fgokibe@yahoo.com

waters and waste from various industrial processes, including steel manufacture, primary aluminium, copper and nickel production, phosphate fertilizer production and use, glass, brick and ceramic manufacturing, and glue and adhesive production (Sloof *et al.,* 1989). The uses of fluoride-containing pesticides as well as the fluoridation of drinking-water supplies also contribute to the release of fluoride from anthropogenic sources (Low and Bloom, 1988).

Fluoride levels in terrestrial biota tend to be increased in areas with high fluoride levels due to both natural and anthropogenic sources. Lichens have been used extensively as biomonitors for fluorides. Davies and Notcutt (1988) sampled lichens from the slopes of the Mount Etna volcano in 1985 and 1987 and found fluoride levels ranging from 2 to 141 mg $Kg^{-1}$ (lichen from control sites contained <2 mg fluoride/kg). Similarly, Davies and Notcutt (1989) found that lichens growing in the Canary Islands accumulated fluorides from minor volcanic eruptions. Fluoride levels of up to 23 mg $Kg^{-1}$ were measured, compared with a background level of <1 mg $kg^{-1}$. Lichens have also been used to monitor anthropogenic outputs of fluorides from both brickfields (Davies, 1982; 1986) and an aluminium smelter (Perkins *et al.,* 1980; 1987). Levels of fluoride were found to be related to site emissions, prevailing winds and distance from source. Mean fluoride concentrations of 150–250 mg $Kg^{-1}$, were measured in lichens growing within 2–3 km of the pollution source. Most of the inorganic fluoride in the soil is insoluble and therefore less available to plants. The capacity for a plant to absorb inorganic fluoride from the soil will also depend on the species of plant and, to some extent, the ionic species of fluoride present in solution (Stevens *et al.,* 1997; 1998a; 1998a).

Fluoride has both beneficial and detrimental effects on human health. The beneficial effects on the teeth and skeleton may be observed at exposures below those associated with the development of other organ- or tissue-specific adverse health effects. Excess exposure to bioavailable fluoride constitutes a risk to aquatic and terrestrial biota Fluoride-sensitive species can be used as medium for the identification of fluoride hazards to the environment. There is a need to improve knowledge on the accumulation of fluoride in organisms and on how to monitor and control this.

The present work became necessary because of the following reasons; the use of Galma river water already established as polluted by Ekanem and Irepita (Ekanem and Irekpita, 2004) for irrigation farming, the all year round application of phosphate fertilizers, the release of effluents into the Galma river and it's tributaries by few industries operating in the study area and the anthropogenic activities within and around the rivers in the study area. This research is with the view of generating a database for fluoride levels in soil and some vegetables grown in some of the irrigation farms on the bank of river Galma, Zaria, Nigeria.

## MATERIALS AND METHOD

***Study Area:***

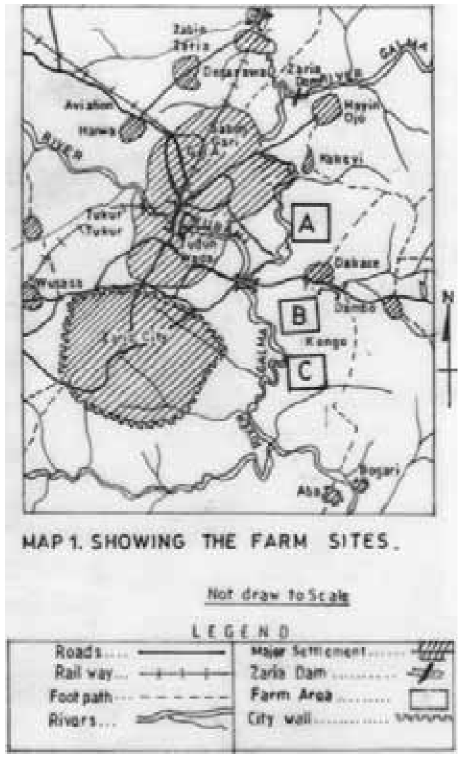
Ekanem and Irekpita (2004) have described the work area in detail in an earlier report. The features in Map 1 critical to the present work are farms A, B and C and River Galma, which receives Kubanni a major river that flows through Zaria metropolis.

***Sample Collection:***

In February 2009 which was the peak of dry season in the tropical climate of the study area, between 9.00am and 12.00noon of the day of sampling, three major farms on the bank of river Galma were identified and coded as farm A, B, and C. In each of the farms, ten (10) samples of soil and the vegetable grown in large quantity were collected by means of random sampling. The vegetables were Cabbage (*Brassica oleracea*), Carrot (*Daucus carota*), and Lettuce (*Lactuca sativa*). The soil and vegetable samples were sealed in clean polythene bags and transported to the laboratory for analysis. During this period of sampling irrigation farming activities, including the application of fertilizers was intense.

***Reagent and Apparatus:***

All reagents used in this work were of analytical grade. Distilled water was used for all dilutions. All glassware were soaked in nitric acid for 24 hrs, rinsed with distilled water before use. Absorbance measurements were performed on a spectrophotometer (thermospectronic, Helios Gama, LR115161, NRTL/C).




MAP 1. SHOWING THE FARM SITES.

***Preparation of Reagent Solution:***
***Standard Fluoride Solution:***

1.5013g ammonium hydrogen difluoride ( $NH_4F.HF$ ) was weighed and dissolved in distilled water and diluted to 1000cm$^3$ . The solution contains 1000mg L$^{-1}$ Fluoride. A serial dilution of the stock solution was prepared in the range 2.0, 4.0, 6.0, 8.0, and 10.0mg L$^{-1}$.

***Alizarin Red Solution:***

0.75g alizarin red was weighed and dissolved in distilled water and made to 1000cm$^3$ in a volumetric flask.

***Zirconyl Acid Solution:***

0.345g of zirconyl Chloride was weighed and dissolved in about 800cm$^3$ distilled water, then 33.30cm$^3$ concentrated $H_2SO_4$ was slowly added and stirred, followed by the addition of 101cm$^3$ HCl, the solution was stirred thoroughly and made up to 1000cm$^3$.

***Sample preparation for Fluoride Determination:***
***Vegetables:***

Using a clean knife, the fresh vegetables harvested from the farms were cut into small pieces. They were left to dry in ambient temperature. The dried samples were crushed into powder using a clean mortar and pestles. 0.5g each of the powdered samples were transferred into about 5.0cm$^3$ concentrated $HNO_3$ in a beaker and heated to near dryness at 100-150$^o$C for six minutes to expel brown gas of $NO_2$. The resulting solution was allowed to cool, dissolved in a little portion of distilled water, and made up to the mark in a 100cm$^3$ volumetric flask.

***Soil:***

The method of partial leaching described by Lori (1987) was applied in the preparation of the soil for analysis. The soil samples were oven dried and crushed to powder. A clean large beaker containing distilled water was exposed to the atmosphere (open air) for 48hrs, stirring after every six hours to allow for maximum absorption of atmospheric gases. 10g each of the oven dried powdered soil samples were separately weighed into a $100cm^3$ glass beaker and $20cm^3$ of the exposed water was added. The mixtures were stirred and allowed to stand for six hours. They were filtered into a $100cm^3$ volumetric flask. The residues were leached slowly over a two-hour period with the same exposed water and filter paper and the leachate going into the same beaker containing the filtrate. The filtrates and the leachate mixture were made to the mark with the exposed water. The exposed water served as the blank in all determination involving the soil samples.

***Spectrometric Determination of Fluoride:***

To $100cm^3$ of both standard and sample solutions were added $5.0cm^3$ each of alizarin red and Zirconyl acid solutions, mixed thoroughly and allowed to strand for one hour for full colour development. Absorbance readings were taken at 520nm. A calibration curve was prepared from the plot of absorbance against concentration of standard solutions. The plot was used to determine the concentration of sample solutions. Where necessary values obtained were multiplied by an appropriate dilution factors to get actual concentrations.

## RESULTS AND DISCUSSION

***Soil Leachable Fluoride:***

Presented in Table 1 are the results of leachable fluoride content in the soils from the three farms investigated. The soil leachable fluoride levels are within the range 0.075 - 0.200 mg $Kg^{-1}$. All the values obtained are well within the range of <0.05 – 1.50 mg $Kg^{-1}$ reported by Gilpin and Johnson (1980) as the water soluble fluoride concentration range for the analysis of 55 clay soil and silt samples in Pennsylvania, USA.

The results is in agreement with data on the levels of total and water soluble fluoride in soil which ranges from 0.02 to 1.00 mg $Kg^{-1}$ in areas without natural phosphate or fluoride deposits as reported by Davison (1983). The mean leachable fluoride concentrations presented in Table 2 for farms A, B, and C were 0.139 ± 0.030, 0.115 ± 0.041, and 0.080 ± 0.005 mg $Kg^{-1}$ respectively. The soil leachable fluoride is important because it is the main factor, which determines the availability of fluoride for plant absorption. If other factors are favourable, the higher the amount the more will be the fluoride available for plant use. Consequently, an increase in the fluoride concentration in the food chain. The soil leachable fluoride from the soils of the farms were in the order farm A > B > C.

The loading of fluoride on the soil arising from the use of the river water for irrigation and fluoride from other sources has no negative effect on the soil, because the soil leachable fluoride is below the 2.57 -16.44 mg $Kg^{-1}$ soil leachable fluoride recommendation of FAO, EPA, and WHO.

**Table 1:** Soil Leachable Fluoride (mg $Kg^{-1}$)

| Soil Sample | Farm A | Farm B | Farm C |
|---|---|---|---|
| 1 | 0.188 | 0.086 | 0.078 |
| 2 | 0.169 | 0.085 | 0.076 |
| 3 | 0.136 | 0.085 | 0.079 |
| 4 | 0.169 | 0.148 | 0.075 |
| 5 | 0.135 | 0.084 | 0.075 |
| 6 | 0.131 | 0.129 | 0.079 |
| 7 | 0.118 | 0.200 | 0.085 |
| 8 | 0.119 | 0.156 | 0.081 |
| 9 | 0.138 | 0.089 | 0.087 |
| 10 | 0.086 | 0.088 | 0.086 |

n = 3

**Table 2:** Statistical Analysis of Data in Table

| 1Soil Sample | Mean (mg $Kg^{-1}$) | S.D.(mg $Kg^{-1}$) | Variance (mg $Kg^{-1}$) |
|---|---|---|---|
| Farm A | 0.139 | ±0.030 | 0.001 |
| Farm B | 0.115 | ±0.041 | 0.002 |
| Farm C | 0.080 | ±0.005 | 2.032 |

***Vegetable Fluoride Content:***

Results for the fluoride contents of all the vegetables analyzed are presented in Tables 3 and 4. The concentration range is 0.013 to 0.129 mg $Kg^{-1}$. The values are significantly lower than the maximum contaminant level of 4.0 mg $Kg^{-1}$ in foods and the level of dose capable of causing illness, which is 0.3 mg $Kg^{-1}$ recommendations of EPA, FAO, and WHO. Normal concentration of fluoride in plant leaves usually range from 0.0001 – 0.015 mg $Kg^{-1}$ [24, 25, 26]. Therefore, the fluoride levels in all the vegetables are within the normal range. The mean fluoride levels in the vegetables follows the order lettuce > cabbage > carrot. The reasons for this order may be in the ability of the plants to accumulate fluoride and the amount of fluoride available for absorption. Comparison of the mean fluoride concentration of the three vegetables using the t-test at 95% confidence level ($p=0.05$) for 18 degrees of freedom, 2.10 critical value, indicated a significant difference between fluoride levels of carrot and cabbage, with $t_{exp}$ = 5.77 which is > 2.10 $t_{critical}$. No significant difference exists in fluoride levels between carrot and lettuce, and lettuce and cabbage both with $t_{exp}$ 1.84 and 1.62 respectively.

**Table 3:** Fluoride Content in Vegetables (mg $Kg^{-1}$)

| Samples | Cabbage (*brassica oleracea*) | Carrot (*daucus carota*) | Lettuce (*lactuca sativa*) |
|---|---|---|---|
| 1 | 0.025 | 0.030 | 0.088 |
| 2 | 0.067 | 0.043 | 0.086 |
| 3 | 0.064 | 0.026 | 0.129 |
| 4 | 0.052 | 0.20 | 0.087 |
| 5 | 0.033 | 0.018 | 0.105 |
| 6 | 0.067 | 0.013 | 0.084 |
| 7 | 0.044 | 0.037 | 0.100 |
| 8 | 0.068 | 0.057 | 0.072 |
| 9 | 0.062 | 0.050 | 0.107 |
| 10 | 0.054 | 0.059 | 0.102 |

n = 3

**Table 4:** Statistical Analysis of Data in Table 3

| Vegetable Sample | Mean (mg $Kg^{-1}$) | S.D.(mg $Kg^{-1}$) | Variance (mg $Kg^{-1}$) |
|---|---|---|---|
| Cabbage *(brassica oleracea)* | 0.054 | ±0.015 | 0.0002 |
| Carrot (*daucus carota*) | 0.035 | ±0.017 | 0.0003 |
| Lettuce (*lactuca sativa*) | 0.096 | ±0.016 | 0.0003 |

Generally, a comparison of soil leachable fluoride and vegetable fluoride content presented in Table 5 indicated a mean total of 0.111 mg $Kg^{-1}$ soil leachable fluoride and 0.061 mg $Kg^{-1}$ mean total fluoride content in vegetable. The reasons why soil leachable fluoride was higher than vegetable fluoride content may be the direct release of natural and anthropogenic fluoride onto the soil while the uptake of fluoride by plant is dependent on a number of factors, soil pH, soil type and type of vegetable.

**Table 5:** Statistical Comparison of Fluorides in Soil and Vegetables

| All Samples | Average of the Means (mg $Kg^{-1}$) | Mean S.D.(mg $Kg^{-1}$) | Variance (mg $Kg^{-1}$) |
|---|---|---|---|
| Soil | 0.111 | ±0.025 | 0.6780 |
| Vegetables | 0.061 | ±0.016 | 0.0027 |

In conclusion, the soil leachable fluoride and vegetable fluoride levels of the soil and some vegetables grown in the three major farms on the bank of river Galma are well below standard limits recommended by EPA, FAO, and WHO. The natural and anthropogenic sources of fluoride to the soil and vegetables have no deleterious effect on them. The consumption of the fresh vegetables from these farms does not pose any treat of fluoride poisoning. However, frequent consumption of these vegetables could contribute significantly to the daily dietary intake of fluoride. We recommend a study of the fluoride levels of the river water used for irrigation and a survey of fluoride content of other vegetables not investigated in this work.

## REFERENCE

Symonds, R., W. Rose and M. Reed, 1988. Contribution of $Cl^-$ and $F^-$ bearing gases to the atmosphere by volcanos. *Nature*, 334: 415-418.

WHO., 1984. Fluorine and fluorides. Geneva, World Health Organization (Environmental Health Criteria 36).

Fuge, R. and M.J. Andrews, 1988. Fluorine in the UK environment. *Environ Geochem Health*, 10(3/4): 96-104.

Kabata-Pendias, A. and H. Pendias, 1984. Fluorine. In: Trace elements in soil and plants. Boca Raton, Florida, CRC Press, pp: 209-215.

Elrashidi, M.A. and W.L. Lindsay, 1986. Chemical equilibria of fluorine in soils. A theoretical development. *Soil Sci*, 141: 274-280.

Weast, R., 1986. CRC handbook of chemistry and physics, 1985–1986. Boca Raton, Florida, CRC Press.

Hart, E.B., P.H. Phillips and G. Bohstedt, 1934. Relationship of soil fertilisation with superphosphates and rock phosphate to the fluorine content of plants and drainage waters. Am J Public Health, 24: 936-940.

McLaughlin, M.J., K.G. Tiller, R. Naidu and D.P. Stevens, 1996. Review: the behaviour and environmental impact of contaminants in fertilizers. *Aust J Soil Res*., 34: 1-54.

Sloof, W., H. Eerens, J. Janus and J. Ros, 1989. Integrated criteria document: Fluorides. Bilthoven, National Institute of Public Health and Environmental Protection (Report No. 758474010).

Low, P.S. and H. Bloom, 1988. Atmospheric deposition of fluoride in the lower Tamar Valley, Tasmania. *Atmos Environ*, 22(9): 2049-2056.

Davies, F.B.M. and G. Notcutt, 1988. Accumulation of fluoride by lichens in the vicinity of Etna volcano. *Water Air Soil Pollut*, 42: 365-371.

Davies, F.B.M. and G. Notcutt, 1989. Accumulation of volcanogenic fluorides by lichens. *Fluoride Q Rep*, 22(2): 59-65.

Davies, F.B.M., 1982. Accumulation of fluoride by *Xanthoria parietina* growing in the Vicinity of the Bedfordshire brickfields. *Environ Pollut*, 29: 189-196.

Davies, F.B.M., 1986. The long-term changes in fluoride content of *Xanthoria parietina* growing in the vicinity of the Bedfordshire brickfields. *Environ Pollut*, A42: 201-207.

Perkins, D.F., R.O. Millar and P.E. Neep, 1980. Accumulation of airborne fluoride by lichens in the vicinity of an Aluminium reduction plant. *Environ Pollut*, 21: 155-168.

Perkins, D.F. and R.O. Millar, 1987. Effects of airborne fluoride emissions near an Aluminium works in Wales: Part 2 — Saxicolous lichens growing on rocks and walls. *Environ Pollut*, 48: 185-196.

Stevens, D.P., M.J. McLaughlin and A.M. Alston, 1997. Phytotoxicity of the Aluminium–fluoride complexes and their uptake from solution culture by *Avena sativa and Lycopersicon esculentum*. *Plant Soil*, 192: 81-93.

Stevens, D.P., M.J. McLaughlin and A.M. Alston, 1998a. Phytotoxicity of the fluoride ion and its uptake from solution culture by *Avena sativa and Lycopersicon esculentum*. *Plant Soil*, 200: 119-129.

Stevens, D.P., M.J. McLaughlin and A.M. Alston, 1998b. Phytotoxicity of hydrogen fluoride and fluoroborate and their uptake from solution culture by *Avena sativa and Lycopersicon esculentum*. *Plant Soil*, 200: 175-184.

Ekanem, E.J. and H. Irekpita, 2004. Determination of pollution Status of Zaria Rivers by physicochemical parameter monitoring. *Chemclass Journal*, 2004: 127-137.

Lori, J.A., 1987. Determination of some essential Minerals in the Source Soil and two cultivars of white yam ( *Discrorea rotundata*).M.Sc thesis, Ahmadu Bello University, Zaria, Nigeria.

Gilpin, L. and A. Johnson, 1980. Fluorine in agricultural soils of southeastern Pennsylvania. *Soil Sci Soc Am J*, 44: 255-258.

Davison, A., 1983. Uptake, transport and accumulation of soil and airborne fluorides by vegetation. In: Shupe J, Peterson H, and Leone N ed. Fluorides: Effects on vegetation, animals and humans. Salt Lake City, Utah, Paragon Press, pp: 61-82.

Cholak, J., 1959. Fluorides: A critical review. I. The occurrence of fluoride in air, food, and water. *J Occup Med*, 1: 501-511.

Cooke, J.A., M.S. Johnson, A.W. Davison and A.D. Bradshaw, 1976. Fluoride in plant colonizing fluorspar mine waste in the Peak District and Weardale. *Environ Pollut*, 11: 10-23.

Hara, T., Y. Sonoda and I. Iwai, 1977. Growth response of cabbage plant to sodium halides under water culture conditions. *Soil Sci Plant Nutr*, 23: 77-84.