J. Basic. Appl. Chem., 1(6)33-38, 2011

ISSN 2090-424X
Journal of Basic and Applied Chemistry
www.textroad.com

Spectrometric Determination of Fluoride in Water, Soil and Vegetables from the Precinct of River Basawa, Zaria, Nigeria

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ABSTRACT

Fluoride levels of water, soil and vegetables from four irrigation farms at the bank of Basawa River, Zaria, Nigeria were estimated using Alizarin red spectrometric method. The soil samples from the four farms had a mean soil leachable fluoride in the range of 0.091 mg Kg^{-1} to 0.135 mg Kg^{-1}, while the river water had mean fluoride levels in the range 0.081 to 0.191 mg Kg^{-1}. The mean concentration of soil leachable fluorides for soils from the farms, at 95% confidence limit, were 0.110 ± 0.011, 0.108 ± 0.001, 0.114 ± 0.012 and 0.108 ± 0.001 mg Kg^{-1} for farms A, B, C and D respectively. At the same confidence limit, the mean fluoride concentration for the river water Upstream, Midstream and Downstream were 0.148 ± 0.027, 0.152 ± 0.036 and 0.137 ± 0.013 mg Kg^{-1}, respectively. T-test was used to evaluate and compare mean values of fluoride in the different vegetables. At 95% confidence interval ($p = 0.05$) and 18 degrees of freedom, with critical value of 2.26, the $|t_{exp}|$ were 0.600, 1.986, 2.649, 1.924, 2.858 and 0.772 for Cabbage and Garden Egg, Cabbage and Onion, Cabbage and Tomato, Garden Egg and Onion, Garden Egg and Tomato and Onion and Tomato respectively. The only significant difference was observed for the fluoride levels of Cabbage and Tomato, and Garden Egg and Tomato where t_{exp} > Critical value. The fluoride values obtained were all below the toxic limit of 2.57 to 16.44 mg Kg^{-1} for soil and maximum contaminant level of 4.0 mg Kg^{-1} for water, food and vegetables as stipulated by the joint EPA, FAO, and WHO Standard limit for fluoride. The implications of the results are discussed.

KEY WORDS: River Basawa, Fluorides, Vegetables, Soil.

INTRODUCTION

The study and monitoring of fluorine and fluorides has been of interest to scientists for a long time. This is because of the reactivity and ready availability of fluorine in many forms. It is the 13^{th} most abundant element of the earth's crust representing about 0.3g / kg. It occurs naturally in the combined state as fluorite (fluorospar), apatite, fluorapatite, topaz and cryolite (Rakshit, 2004).

Fluoride pollution in the environment is usually from two channels; natural and anthropogenic (Cengeloglu *et al,*. 2002). Natural Fluoride is frequently encountered in minerals and in geochemical deposits and is generally released into subsoil water sources by slow natural degradation of fluorine contained in rocks (WHO, 1984). Anthropogenic sources include human activities like industrialization, mechanization, use of fluoride containing pesticides and the fluoridation of drinking water supplies (Low and Bloom, 1988). In many parts of the world there is an inverse relationship between the fluoride content of drinking water and the amount of dental carries in the population. The fluoridation of public water supplies to a level of about 1.0 mg dm^{-3} is now relatively common (Campbell, 1987). It is however very important to carefully monitor the levels of fluoride because of the attendant health risks associated with high fluoride levels in drinking water and indeed foods. Ingestion of high levels of fluoride can lead to mottling of the teeth and bone density deterioration among others. The presence of fluorides in industrial effluents must also be monitored. Fluoride is released into the environment via exhaust fumes, process waters and waste from various industrial processes, including steel manufacture, primary aluminum, copper and nickel production, phosphate fertilizer production and use, glass, brick and ceramic manufacturing, and glue and adhesive production (Sloof *et al.,* 1989).

Manufacture of phosphate fertilizers is one major industrial source of fluoride. The fertilizer is made from rock phosphate which contains about 3.5% fluorine (Okibe *et al* 2010). However this percentage is further reduced to between 1.3 and 3% in the manufacturing process (McLaughlin *et al.*, 1996). Irrigation activities around the banks of the Basawa River go on almost all year round and this involves the application of large amounts of fertilizers to the farms. In addition to some other possible sources, fluorides from the applied fertilizers are leached into the soil from where they find their way into the river water as well as the plants cultivated there. Many plants are known to be quite sensitive to fluoride

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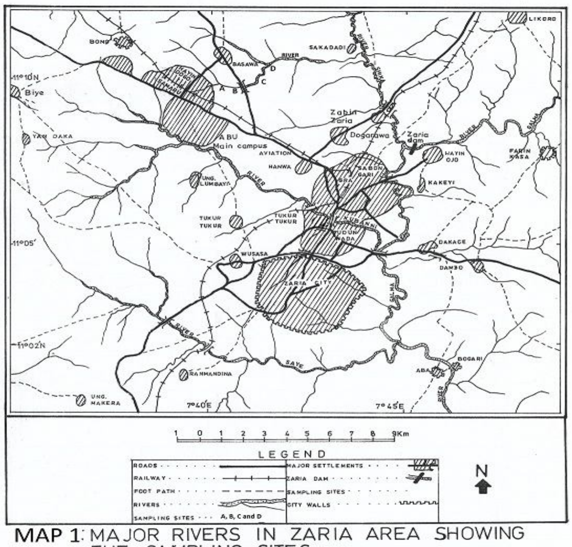
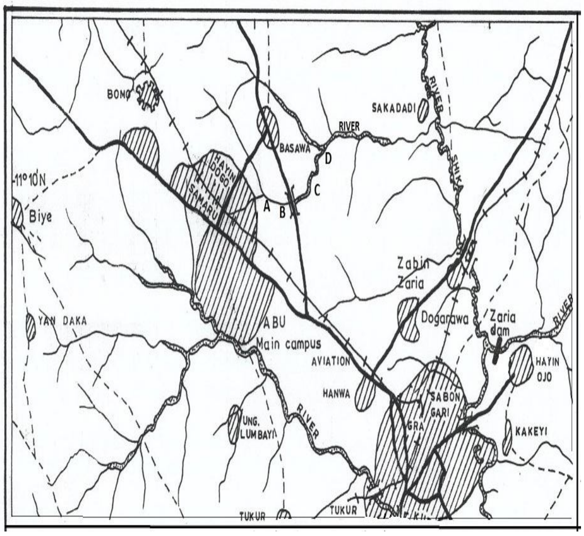
while others, like the tea plant, are known fluoride accumulators (Campbell, 1987). Lichens have also been used extensively as bio-monitors for fluorides (Davies, 1982; 1986). Available data from lichens growing around areas with volcanic activities indicate high fluoride levels of up to 141 mg Kg^{-1} (Davies and Notcutt, 1988).

Mean fluoride concentrations of 150–250 mg Kg^{-1}, have also been measured in lichens growing within 2–3 km of pollution sources. However, most of the inorganic fluoride in the soil is insoluble and thus not readily available for uptake into the plants. The ability and extent to which a plant can absorb inorganic fluoride from the soil depends on the plant species and the nature of the ionic species of fluoride present in solution (Okibe *et al.*, 2010; Stevens *et al.,* 1997; 1998a; 1998b).

The biotas of tropical areas are the richest of all. However it is imperative to monitor and shield such populations from the adverse effects of human and natural activities where possible, in order to maintain the delicate balance of the eco system. The evaluation of fluorides in plant species can be used as a marker for the possible fluoride hazards to the environment. The need to develop a data bank of fluoride contents of plants especially those grown in areas where anthropogenic activities is significant, cannot be overemphasized. A nebulous and vague representation of such will only leave the population in danger of deleterious health effects.



MAP 1: MAJOR RIVERS IN ZARIA AREA SHOWING THE SAMPLING SITES.
SOURCE :- Topographic map of Zaria sheet 102 and field survey 2005



MAP 2: ENLARGED MAP OF THE SAMPLING SITE

MATERIALS AND METHOD

Study Area:

The study area has been extensively described in an earlier report (Ekanem and Irekpita, 2004). Map 1 gives a general overview of the area immediately surrounding the study area. It shows the major rivers in Zaria area. Map 2 gives a closer view of the Basawa River and the sampling sites.

Sample Collection:

Samples from four major farms at the bank of River Basawa, labeled Farm A, Farm B, Farm C and Farm D, were collected between 7am and 11am. Ten samples of Soil and vegetables were collected from each farm by means of random sampling. Ten samples of the river water were also collected from Upstream, Midstream and Downstream each. The water samples were collected in sealed plastic cans. The vegetables sampled were Cabbage (*Brassica oleracea*), Garden egg (*Solanum ovigerum)*, Onion *(Allium Cepa)* and Tomato *(Lycopersicon Esculentum)*. The soil and vegetable samples were sealed in clean polythene bags. All the samples collected were transported to the laboratory for analysis. Irrigation activities and the application of fertilizers were intense at the time of sampling.

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 and dried before use. Absorbance measurements were performed on a spectrophotometer (Thermospectronic, Helios Gama, LR115161, NRTL/C).

Preparation of Reagent Solution:

Standard Fluoride Solution:

1.5013 g ammonium hydrogen difluoride (NH4F.HF) was weighed and dissolved in distilled water and diluted to 1000 cm^3. The solution contains 1000 mg L^{-1} Fluoride. A serial dilution of the stock solution was prepared in the range 2.0, 4.0, 6.0, 8.0, and 10.0 mg L^{-1}.

Alizarin Red Solution:

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

Zirconyl Acid Solution:

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

Sample preparation for Fluoride Determination:

Vegetables:

The fresh vegetables harvested from the four farms were cut into small pieces and dried at room temperature. They were then ground into powder with a clean mortar and pestle. To 0.5g each of the powdered samples were added 5.0cm^3 of concentrated HNO_3 in a beaker and heated to near dryness at 150 ^{0}C for six minutes to expel brown gas of NO_2. The resulting solution was allowed to cool, dissolved in a small portion of distilled water, and made up to the mark in a 100cm^3 volumetric flask.

Soil:

The method of partial leaching employed in the preparation of the soil for analysis has been described (Lori, 1987). The soil samples were dried in an oven and crushed to finer particles, and 10g each of the dry powdered soil samples was weighed into sealed bottles. A large beaker containing distilled water was allowed to stand on the bench for 48 hours with regular stirring at 6 hours intervals allowing maximum absorption of atmospheric gases.

20cm^3 of the exposed water was then mixed with each of the 10 g soil samples. The mixtures were stirred and allowed to stand for another 6 hours, and then filtered into 100cm^3 volumetric flasks. The residues were then leached into the same beaker containing the filtrate over a period of two hours using the exposed water. This was then made to the mark with the exposed water. The exposed water was used as blank in all determination involving the soil samples.

Spectrometric Determination of Fluoride:

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

RESULTS AND DISCUSSION

Soil Leachable Fluoride:

Results of the soil leachable fluorides for the soil samples from farms A, B, C and D are presented in Table 1. Table 2 gives the statistical analysis of the data in Table 1. The investigation found the soil leachable fluoride to be in the range of 0.091 to 0.135 mg Kg^{-1}. The averages for Farm A, B, C and D respectively, are 0.110 ± 0.011, 0.108 ± 0.001, 0.114 ± 0.012 and 0.108 ± 0.001 mg Kg^{-1}. The amount of fluoride in Farm C was greater than that in Farm A which in turn is greater than that in Farms B and D. Farm B and D were found to have equivalent amounts of fluoride in their soils [Farm C>A>(B=D)]. All these are well below the maximum of 1.50 mg Kg^{-1} reported by Gilpin and Johnson (Gilpin and Johnson, 1980) and between 0.02 to 1.00 mg Kg^{-1} as reported by Davidson (Davidson, 1983). The values are also within the range of 0.075 to 0.200 mg Kg^{-1} as obtained by Okibe et al. (Okibe et al., 2010). The soil leachable fluoride is an indication of the amount of fluoride that will be available for plants and other organisms in the immediate environment. Thus a high value of this parameter indicates that the plants are more likely to absorb more fluoride from the soil, and vice versa.

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

Soil Sample	Farm A	Farm B	Farm C	Farm D
1	0.122	0.099	0.117	0.106
2	0.111	0.129	0.126	0.103
3	0.105	0.109	0.106	0.104
4	0.108	0.107	0.098	0.106
5	0.104	0.106	0.108	0.107
6	0.135	0.109	0.132	0.091
7	0.107	0.104	0.103	0.105
8	0.103	0.098	0.103	0.121
9	0.096	0.104	0.119	0.110
10	0.104	0.116	0.130	0.127

Table 2: Statistical Analysis of Data in Table 1:

	N	Minimum	Maximum	Mean	Std. Deviation	Variance
Farm A	10	0.096	0.135	0.10950	0.011168	0.00012
Farm B	10	0.098	0.129	0.10810	0.008975	0.00008
Farm C	10	0.098	0.132	0.11420	0.012273	0.00015
Farm D	10	0.091	0.127	0.10805	0.009880	0.00009
Valid N (listwise)	10					

Fluoride Content of River Water:

The results for the fluoride content of the river water analyzed are presented in Table 3. Table 4 gives the summary of the statistical analysis of the results in Table 3. The mean fluoride content ranged from 0.81 to 1.91 mg Kg^{-1}. The mean fluoride content for the three locations were 0.148±0.027, 0.152±0.036 and 0.137±0.013 mg Kg^{-1} for upstream, midstream and downstream respectively. The mean fluoride content were in the order Midstream>Upstream>Downstream. The results are below the standard limits recommended by WHO, EPA and FAO. It has been reported that the presence of some rocks (like limestone) can help reduce the amount of phosphates and fluorides in underground water (Svetlana, 2004). It is possible that such reactions can be taking place in the path of the river only for the rigorous application of fertilizers to compensate for any loss in fluorides at midstream (AbuZeid and ElHatow, 2008; Jakovljević et al., 2002).

Table 3: Fluoride Content of River Water (mg Kg^{-1})

Water Sample	Upstream	Midstream	Downstream
1	0.161	0.081	0.154
2	0.143	0.163	0.118
3	0.164	0.156	0.137
4	0.105	0.098	0.149
5	0.162	0.143	0.123
6	0.101	0.184	0.154
7	0.152	0.178	0.147
8	0.161	0.154	0.126
9	0.145	0.167	0.133
10	0.186	0.191	0.127

Table 4: Statistical Analysis of Data in Table 3

	N	Minimum	Maximum	Mean	Std. Deviation	Variance
Upstream	10	0.101	0.186	0.14800	0.026546	0.00070
Midstream	10	0.081	0.191	0.15150	0.035936	0.00129
Downstream	10	0.118	0.154	0.13680	0.013398	0.00018
Valid N (listwise)	10					

Fluoride Content of Vegetables

Results for the fluoride contents of all the vegetables analyzed are given in Table 5, while the statistical analysis is given in Table 6. The concentration ranged between 0.013 and 0.065 mg Kg^{-1}. The mean vegetable fluoride contents were 0.033±0.0086, 0.030±0.0117, 0.041±0.0119 and 0.046±0.0125 mg Kg^{-1} for Cabbage, Garden egg, Onion and Tomato respectively, and were in the order Tomato > Onion > Cabbage > Garden egg. These values are much lower than the daily toxic dose level of 0.30 mg Kg^{-1} and the allowed level of 4.00 mg Kg^{-1} recommended by WHO, EPA and FAO. Most plants have their fluoride level within the range 0.0001 to 0.015 mg Kg^{-1} (Okibe et al., 2010). The fluoride content in all the vegetables were observed to be higher this. However, this can be an indication that the selected vegetables are good fluoride accumulators, or that the amount absorbed by the plants is proportional to the fluoride contents of the soil and water.

Table 5: Fluoride Content of Vegetables (mg Kg^{-1})

Sample	Cabbage *(Brassica Oleracea C.)*	Garden Egg *(Solanum ovigerum)*	Onion *(Allium Cepa)*	Tomato *(Lycopersicon Esculentum)*
1	0.028	0.041	0.041	0.061
2	0.037	0.019	0.054	0.027
3	0.026	0.036	0.028	0.048
4	0.022	0.043	0.046	0.036
5	0.045	0.027	0.035	0.029
6	0.034	0.014	0.052	0.052
7	0.040	0.028	0.061	0.049
8	0.028	0.045	0.037	0.048
9	0.027	0.032	0.023	0.043
10	0.047	0.013	0.037	0.065

Table 6: Statistical Analysis of Data in Table 5

	N	Minimum	Maximum	Mean	Std. Deviation	Variance
Cabbage	10	0.022	0.047	0.03340	0.008566	0.00007
Garden Egg	10	0.013	0.045	0.02980	0.011708	0.00013
Onion	10	0.023	0.061	0.04140	0.011900	0.00014
Tomatoe	10	0.027	0.065	0.04580	0.012461	0.00016
Valid N (listwise)	10					

Paired Samples Test:

As presented in Table 7, a comparison of the mean fluoride concentration of the four vegetables using t-test at 95% confidence level ($p = 0.05$) for 18 degrees of freedom, and critical value, $t_{critical} = 2.26$ indicate a significant difference for the fluoride levels of the Cabbage and Tomato, and the Garden egg and Tomato pairs, where $t_{exp} = 2.649$ and 2.858 respectively, both > 2.26 $t_{critical}$. There was no significant difference between the fluoride levels of Cabbage and Garden egg, Cabbage and Onion, Garden egg and Onion, and Onion and Tomato pairs, where the t_{exp} were 0.600, 1.986, 1.924, and 0.772 respectively.

Table 7: Comparison of Means of Vegetable Fluoride Contents (t – test)

		Paired Differences					t	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference			
					Lower	Upper		
Pair 1	Cabbage-Garden Egg	0.003600	0.018981	0.006002	-0.009978	0.017178	0.600	0.563
Pair 2	Cabbage – Onion	-0.008000	0.012737	0.004028	-0.017111	0.001111	-1.986	0.078
Pair 3	Cabbage – Tomato	-0.012400	0.014804	0.004681	-0.022990	-0.001810	-2.649	0.027
Pair 4	Garden Egg – Onion	-0.011600	0.019062	0.006028	-0.025236	0.002036	-1.924	0.086
Pair 5	Garden Egg – Tomato	-0.016000	0.017701	0.005598	-0.028663	-0.003337	-2.858	0.019
Pair 6	Onion – Tomato	-0.004400	0.018014	0.005696	-0.017286	0.008486	-0.772	0.460

A Comparison of the averages of the means of the soil, water and vegetables as given in Table 8, shows a mean total of 0.110±0.011 mg Kg^{-1}soil leachable fluoride, 0.145±0.025 mg Kg^{-1} mean total water fluoride content and 0.038±0.011 mg Kg^{-1} mean total vegetable fluoride content. The higher fluoride content of the soil and water is expected since the sources of fluoride contamination affect them first. The amount of fluoride in the plant depends on their ability to absorb the fluoride from the soil. This in turn depends on whether the fluoride is in an available state for uptake or not.

Table 7: Statistical Comparison of Fluorides in Water, Soil and Vegetables

Samples	Averages of Means (mg Kg^{-1})	Mean Standard Deviation (mg Kg^{-1})	Variance (mg Kg^{-1})
Soil	0.1100	±0.0106	0.00011
Water	0.1454	±0.0253	0.00072
Vegetables	0.0376	±0.0112	0.00013

In conclusion, the results show that the use of the Basawa river water for irrigation has no deleterious effect on the soil and vegetables cultivated at the precinct of the river. Also, the contribution of fluoride to the soil, river water and vegetables from anthropogenic sources within and around the Basawa river area is not ultimately damaging to human health. But caution must be employed in the utilization of the crops as continuous ingestion may result in considerable increase in the daily dietary intake leading to deleterious bioaccumulation in the human body.

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