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Estimation of Fluoride Concentration in Vegetations in Ikot Abasi, Akwa Ibom State,Nigeria

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Abstract
A survey of fluoride contents of certain fodder plants like cassava, bitterleaf and wire grass at close locations around aluminium smelting company in Ikot Abasi , Nigeria, were conducted in July , October and November , 2010 and July, October and November, 2011 .The fluoride contents of the vegetations obtained in this study were compared with the background fluoride content in vegetations determined elsewhere around the aluminium smelting plant before the commissioning of the plant . From the results of this study, the fluoride contents in vegetations considered were far higher than the background fluoride contents of less than 2 mg/kg . Fluoride content in cassava increased by 200 % , bitterleaf increased by 300 % in 2010, and fluoride content in cassava increased by more than 1000 % , wire grass increased by 200 % and bitterleaf increased by 500 % in 2011. As has been suggested that the daily fluoride intake should not exceed 10 mg per person, there is the need to set up bio-indicator systems for routine monitoring of fluoride emissions and control around the smelting plant.
Keywords : Fluoride , Aluminium smelting, Vegetation, Fluorosis , Phytotoxic.

1. Introduction

Fluorine is the 13th most abundant element in the earth's crust (about 625 mg/kg) and exists in trace amount in almost all ground waters , soil and air throughout the world (Annette, 2008) .

Exposure of vegetations mostly leaves, to high fluoride concentration causes yellowing of the leaves and necrosis (dead body) . Fluoride-induced symptoms have been described in many reviews (WHO, 1984; Canady et al , 1993; McDonald and Berkeley,1969; EPA, 1980; Thompson et al, 1971).

One source of fluoride pollution is gaseous fluoride emitted from aluminum smelters . Ikot Abasi has an aluminium smelting plant established more than fifteen years with an installed capacity of 190,000 metric tons of primary aluminium per annum (ALSCON, 1997) .

Gaseous fluoride enters the leaf through the stomata , then it dissolves in the water permeating the cell walls(IPCS, 2002). Regarding aluminum smelters, the fluorine emission to be expected is a primary consideration, the continuous control of which must be ensured. Certain fluorine connections as has been established are highly phytotoxic ; when being fed with polluted fodder , livestock will indirectly suffer health damages - fluorosis (Knosel, 1992 ; Less, L. N, 1975; Occupational Safety and Health Series, 1980) .More detailed experiences and literature are not available regarding the danger to human beings.

Drinking water and edible vegetation are often the sources of fluoride intake by humans especially in areas where fluoride concentration in ground water /or surface water and air are high (Jaffery et al, 1998 ; Edmunds and Smedley,2005; Telde-Halmanot el al, 2006) . Apart from the fact that more than 200 million people worldwide rely on drinking water with fluoride concentration that exceeded the present WHO guidelines of 1.5 mg/l (WHO, 2004) , in some areas foodstuffs and /or indoor air pollution due to the burning of coal may make a significant contribution to the daily intake of fluoride (Nielsen and Dahl,2002 ; Ando et al , 2001). Excess fluoride intake causes different types of fluorosis primarily dental and skeletal fluorosis depending on the level and period of exposure (IPCS, 2002).

In a given locality , anthropogenic activities such as aluminium smelting , power generation and application of phosphate containing fertilizers , may contribute considerable amount of fluoride into the environment (Saxena and Ahmed, 2003). Ikot Abasi is an area of intense anthropogenic activities like aluminium smelting, power generation using fossil fuel and cement production. The extent of fluoride contamination in the air in Ikot Abasi has not been studied , and a little is known about the incidence of fluorosis , necrosis and yellowing of leaves . However,

preventive measures are likely to be required in this regard.
This present study is aimed at the determination of fluoride absorption by leaves in Ikot Abasi as an estimation of fluoride contamination of air around the anthropogenic sources in the area. For opinions on fluorine intoxications it is decisive to know , how much of the quantity emitted is finally absorbed by fodder (plants), which will ultimately be taken in by humans as food. It has been suggested that daily fluoride intake should not exceed 10 mg per person (Institute of Medicine, 1997). In this connection, bio-indicator systems have proved successful (Knosen, 1992).
The fluoride contents of the vegetations will be determined by fluoride ion selective electrode, which is fast, economical and a precise tool to determine fluoride contents in plant, liquid, food and soil samples (Tsyr-Horny et al, 2008) .

2. The Study Area
Ikot Abasi Local Government Area is one of the thirty-one local government areas in Akwa Ibom State, in southern Nigeria . Ikot Abasi lies near the mouth of Imo River , at geographical coordinates $4^0\ 4^{|}0^{||}$ North , $7^0\ 55^{|}\ 0^{||}$ East. Ikot Abasi is situated at a break in the mangrove swamps and rain forest of the eastern Niger River Delta (Figure 1). It is bordered by Oruk Anam Local Government Area in the north , Mkpat Enin Local Government Area in the west and Eastern Obolo Local Government Area on the Atlantic Ocean in the south (ALSCON, 1997).
The region is flat and low-lying , but three major physiographic units can be identified from the terrain, the alluvial plains (mangrove and flood plains), the beach ridge sands and the rolling sandy plains (ALSCON, 1997).
The geological formations in the area consist of the Quaternary sedimentary deposits, and the Tertiary Coastal Plain Sands, generally referred to as Calabar Formation. The Quaternary sediments give rise to alluvial plains as well as the beach ridge sands. The alluvial plains include mangrove mudflats, which are under the influence of tidal brackish waters along the coast and in the estuaries of rivers and creeks.
The flood plains and inter tributary areas have light grey to dark carbonaceous mud and clay. The tertiary Coastal Plain Sand , or Calabar Formation is older and consists of beds of unconsolidated coarse textured sandstones , inter- bedded with layers of fined grained massive clay (ALSCON, 1997).
The most important soils in the area are those, developed on Tertiary Coastal Plain Sands in the upland part of the local government area. The soils are deep , have loamy sand to sandy loam surface over clay loam to sandy clay subsoil. The soils are acidic and are generally referred to Acid Sands. They are well drained and strongly weathered.
The climate of the area is that of humid tropic . Temperatures are high , lying between 26 ^{o} C and 28 ^{o} C , rainfall is heavy and the mean annual rainfall lies between 2000 mm to 4000 mm. The rainy season lasts from April to November and is characterized by high relative humidity , while the dry season proper begins in November and ends in March (ALSCON, 1997). These factors and the decreasing salt content of the upland mainly determine the composition of the species of the vegetation; it must be considered that as a result of the dense population of the rain forest zone, the agricultural utilization is intensive, which also applies to the surroundings of the site.
The locations selected and the various plants leaves sampled from the study area are listed in Table 1.

3. Materials and Methods:
Leaves of selected plants namely, cassava, bitterleaf and wiregrass (Table 1) , were collected in polyethylene bags. The leaves were oven-dried at 105^0 C and the fluoride concentration determined by the methods of McQuaker, 1977 and AOAC, 1997 . The dried vegetations were crushed into powdered form using vegetable crusher. To a nickel crucible was added 5 gram of the ground samples and 15 ml of lime suspension (6 gram calcium hydroxide in 300 ml water). The nickel crucible with sample mixture was fired in a furnace for two hours at 660 ^{o} C , with furnace door slightly opened. The sample was removed from furnace , about 8 gram of NaOH pellets added and put back into the furnace for 15 minutes .
The sample digest was removed from furnace, allowed to cool and some deionised water added to dissolve the melt. The digest was steam distilled with 50 ml of concentrated perchloric acid below 150 ^{O} C into 500 ml polyethylene volumetric flask (about 400 ml) and make up to the mark with de-ionized water. Fluoride contents of the distillates was determined by the use of ion selective meter with fluoride electrode (ATI Orion 940) . Total ionic strength adjuster buffer (TISAB) was mixed on a 1: 1 basis with an aliquot (10 ml) of the distillate before reading the fluoride content with the instrument (Colina et al, 1990).
Vegetation sampling was conducted in July, October and November of 2010 and repeated in July, October and November 2011.

4. Results and Discussion

The results of fluoride analysis in vegetations around ALSCON Plant in Ikot Abasi are presented in Tables 2 and 3, and graphically presented in Figures 2 and 3.

In July, October and November , 2010, the vegetations sampled gave mean fluoride concentrations of 0.452 mg/kg to 6.455 mg/kg (Table 2). The lowest fluoride concentration of 0.343 mg/kg was obtained in July , 2010, in Cassava at Akwa Ibom State Industrial Estate (about 300 metres from ALSCON). The highest fluoride concentration of 6.812 mg/kg was obtained in October 2010, in Bitterleaf , at Ikot Obong Village (Table 2 and Fig.2). These results are comparable to the background fluoride concentration of 2 mg/kg in vegetations around ALSCON Plant earlier reported (Knosel, 1992).

In July, October and November, 2011, the vegetations sampled gave mean fluoride concentrations of 4.124 mg/kg to 41.05 mg/kg (Table 3). The lowest fluoride concentration obtained with the period under consideration was 2.452 mg/kg in November , 2011 in Wire grass at Berger Camp. Also, the highest fluoride concentration of 46.69 mg/kg was obtained in November, 2011 , in Cassava at ALSCON Access Road (Figs . 2 and 3). Comparatively, these values are higher than the background fluoride concentrations of less than 2mg/kg reported in vegetations around ALSCON Plant (Knosel, 1992; ALSCON, 1997).

From the results, there is fluoride burden in vegetations around the Aluminium smelter and within the study area there is no other identifiable source of fluoride emission. ALSCON Plant started production in 1998 and was shot down in 1999, and under a new investor started production again in 2008 till date. Therefore, fluoride emission to be expected should be a primary consideration, the continuous control of which must be ensured by effective working of the fume –treatment units.

Although, there is an enhanced concentration of fluoride in vegetations around the smelting plant in the study area (Figures 2 and 3) , the mean values are still lower than mean levels of fluoride in vegetation near large sources of fluoride emission that ranged from 281 mg/kg (severely damaged areas) to 44 mg/kg in slightly damaged areas reported elsewhere (http://www.greenfacts.org/).

Evidence shows that the smaller the distance from high fluoride sources such as aluminium smelters or phosphorus plants , the higher the fluoride levels in soils/ air and hence the degree of damage to vegetation.

5. Conclusion

The results of the study indicated that the background fluoride concentration of 2mg/kg in the vegetations around aluminium smelting company have been far exceeded (Tables 2 and 3) .Fluoride content in cassava increased by 200 % , bitterleaf increased by 300 % in 2010, and fluoride content in cassava increased by more than 1000 % , wire grass increased by 200 % and bitterleaf increased by 500 % in 2011. As has been suggested that the daily fluoride intake should not exceed 10 mg per person,since these vegetations are used as food by the local population, there is the need to set up bio-indicator systems for routine monitoring of fluoride emissions and control around the smelting plant.

As noted elsewhere (Knosel, 1992) there was certainly no immediate cause to assume that a previous fluoride burden around the study area-Ikot Abasi existed before the commissioning of the aluminium smelter. Therefore, the enhanced fluoride concentration in the studied vegetations is attributed completely to the aluminium smelting operations. Considering the phyto -toxicity of fluoride, it is appropriate to set-up bio-indicator measuring system in the area to routinely monitor the intake of fluoride by plants in the study area. More so, due to the location of the aluminium smelter at the coastal area close to the Atlantic ocean (about 12 nautical miles) , whereby the in-ward driving wind of the atlantic ocean ferries fluoride particulates from smelter emissions directly on the coast and the hinterland.

From the results, fluoride concentration at all the locations are higher than the background concentrations , which may be appropriate to recommend a further study to estimate the fluoride concentration in the surrounding air and the soils around the smelter, to ascertain the route of fluoride intake in the fodders in the area.

As indicated by the results of the study using bio-indicator systems, the smelting activities have greatly impacted on the local environment, and therefore, there is an urgency to control the emission of fluoride from the aluminium smelter, since there is no other suspected source of contamination.

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Dr Usoro Monday Etesin was born in Ikpa Ibekwe in April 26, 1964 , and hails from Ikot Akpanata Village in Ikpa Ibekwe Clan of Ikot Abasi Local Government Area .

He attended Primary School Ikot Obong , Ikpa Ibekwe , Ikot Abasi Local Government Area, where he obtained a First School Living Certificate in 1974 at Merit level. He later attended Methodist Secondary School Ete , Ikot Abasi , where he obtained a GCE (O/L) in 1981 . He proceeded to Federal University of Technology Owerri , in 1983 , where he obtained Bachelor of Science Technology degree in Industrial Chemistry in 1988 at First Class level .

Having completed the mandatory one year National Youth Service in 1989, worked briefly with Dresser Magcobar .Port Harcourt as a Laboratory Technologist. In 1990, proceeded to do a Master of Science degree in Analytical Chemistry with the University of Port Harcourt and graduated with the degree in 1992.

He later joined the services of the Department of Chemistry ,University of Calabar as an Assistant Lecturer in 1994 . He was later promoted to Lecturer II in 1996 . Whilst , with the services of University of Calabar , enrolled for a Doctor of Philosophy degree in Analytical Chemistry in 1996, and was awarded the Doctor of Philosophy degree in Analytical / Environmental Chemistry in 2003 by the University of Calabar.

In July 2010, he joined the services of Akwa Ibom State University , Mkpat Enin , as Lecturer I in the Department of Chemistry , and was appointed the Pioneer Acting Head , Department of Chemistry.

Dr Usoro Etesin has his hobbies as reading , table tennis , photography and athletic .

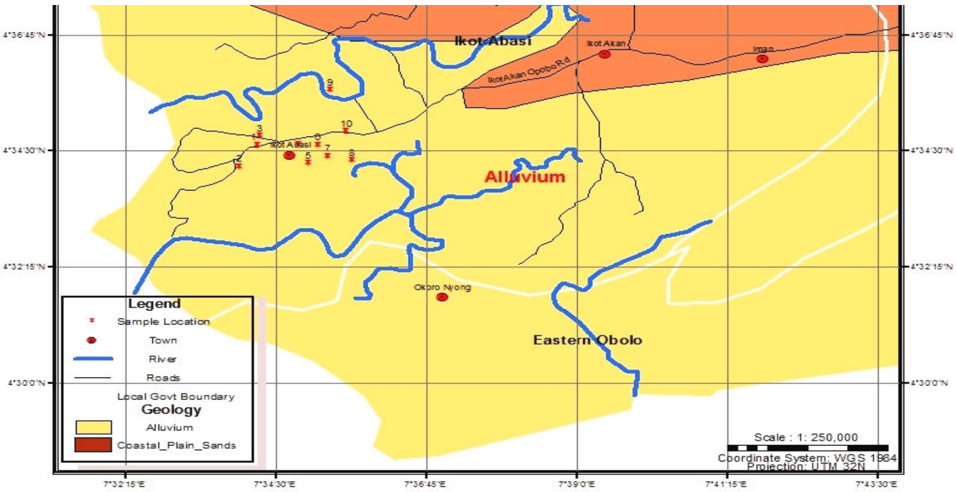

Figure. 1: Map of Ikot Abasi showing sample locations

Table 1 : Showing location of sample and type of vegetation .

S/N	Location	Type of vegetation	Description
1	Ikot Etetuk Village Square	Cassava	Close to ALSCON Plant
2	Federal Housing Estate	Cassava	Behind ALSCON Plant
3	ALSCON Estate(Berger Camp)	Wire grass	300 metres , East of ALSCON
4	ALSCON Access Road	Cassava	North of Casthouse
5	Primary School , Ikot Obong	Cassava	Behind ALSCON
6	Ikpetim Village	Bitterleaf	West of ALSCON
7	South of Potroom	Cassava	60 metre from ALSCON
8	Ikot Obong Village Square	Bitterleaf	1km from ALSCON
9	Akwa Ibom Industrial Estate	Cassava	East of ALSCON
10	Berger Jetty	Cassava	300 metres from ALSCON

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Table 2 : Fluoride content in vegetation in 2010

S/N	Location	Type of vegetation	Fluoride content (mg/kg)			
			July,2010	October,2010	November, 2010	Mean
1	Ikot Etetuk Village Square	Cassava	1.635	1.961	1.973	1.855
2	Federal Housing Estate	Cassava	4.561	5.022	4.992	4.857
3	ALSCON Estate(Berger Camp)	Wire grass	0.672	0.843	0.912	0.808
4	ALSCON Access Road	Cassava	1.702	1.788	1.792	1.761
5	Primary School , Ikot Obong	Cassava	1.99	1.977	1.946	1.971
6	Ikpetim Village	Bitterleaf	6.682	6.812	5.871	6.455
7	South of Potroom	Cassava	1.552	1.903	1.875	1.776
8	Ikot Obong Village Square	Bitterleaf	3.641	3.672	3.802	3.705
9	Akwa Ibom Industrial Estate	Cassava	0.343	0.516	0.498	0.452
10	Berger Jetty	Cassava	0.899	1.022	1.052	0.991

Table 3 : Fluoride content in vegetation in 2011

S/N	Location	Type of vegetation	Fluoride content (mg/kg)			
			July,2011	October,2011	November, 2011	Mean
1	Ikot Etetuk Village Square	Cassava	19.59	24.81	15.26	19.89
2	Federal Housing Estate	Cassava	11.37	7.033	7.731	8.711
3	ALSCON Estate(Berger Camp)	Wire grass	5.825	4.095	2.452	4.124
4	ALSCON Access Road	Cassava	39.04	37.43	46.69	41.05
5	Primary School , Ikot Obong	Cassava	6.794	4.431	3.271	4.832
6	Ikpetim Village	Bitterleaf	9.815	11.45	13.3	11.52
7	South of Potroom	Cassava	34.28	30.55	25.45	30.09
8	Ikot Obong Village Square	Bitterleaf	7.019	6.259	7.821	7.033
9	Akwa Ibom Industrial Estate	Cassava	6.254	8.352	8.511	7.706
10	Berger Jetty	Cassava	8.293	9.755	8.209	8.752

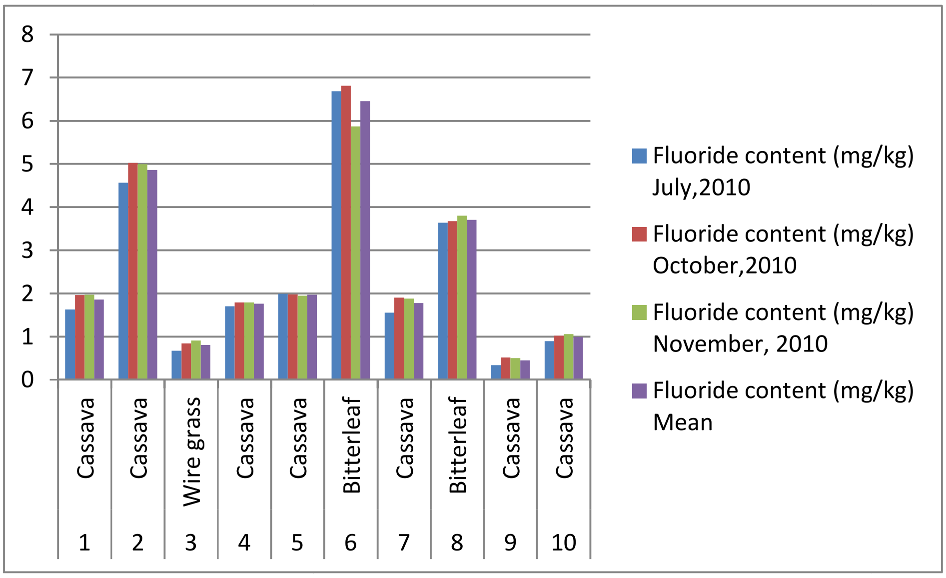

Figure 2: Bar Chart representation of fluoride content in 2010

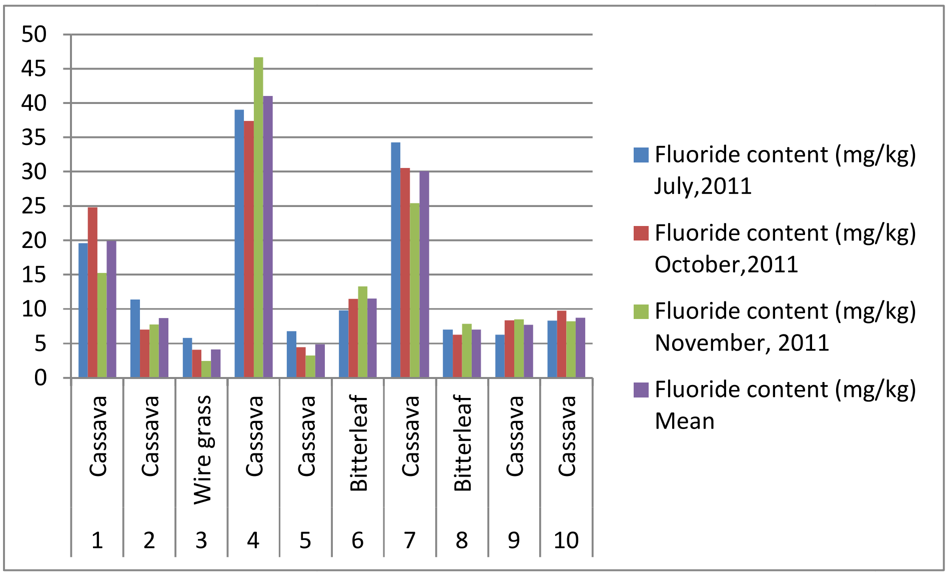

Figure 3 : Bar chart representation of fluoride content in 2011