Open Journal of Soil Science, 2014, 4, 388-398
Published Online November 2014 in SciRes. http://www.scirp.org/journal/ojss
http://dx.doi.org/10.4236/ojss.2014.411039

Scientific Research

Fluoride Uptake and Net Primary Productivity of Selected Crops

P. C. Mishra*, S. K. Sahu, A. K. Bhoi, S. C. Mohapatra

Department of Environmental Sciences, Sambalpur University, Jyoti Vihar, Sambalpur, Odisha, India
Email: *profpcmishra@gmail.com

Received 18 September 2014; revised 15 October 2014; accepted 26 October 2014

Academic Editor: P. V. V. Prasada Rao, Andhra University, India

Abstract

Crop field soil collected from Sambalpur University campus of Odisha and treated with various fluoride concentrations was used to raise selected local crops. Background concentration of total and leachable fluoride content in soil was 95.19 and 8.89 ppm respectively. At the time of harvest of the crops, the total fluoride content was found to decrease and leachable fluoride content was found to increase both in control and experimental sets. This might be due to the addition of fluoride to soil in the experimental set up as well as availability of background fluoride content in soil and the irrigated water (*i.e.* 0.5 ppm). The fluoride accumulation in plant tissue increased with increase in the fluoride content in soil. Net Primary Productivity (NPP) of fluoride treated plants decreased in Brinjal by 6.64% - 56.72%, Tomato by 14.46% - 62.24% and Mung by 10.27% - 53.61%, all in 20 - 100 ppm fluoride range. However, NPP of Mustard, Ladies finger and Chili decreased by 15.58% - 61.21%, 12.28% - 52.78% and 40.8% - 90.65% in 10 - 50 ppm fluoride treated sets respectively in 10 - 50 ppm fluoride range. Maize NPP decreased by 12.17% - 61.20% in 20 - 100 ppm fluoride range as Rice NPP decreased by 6.64% - 56.72% in 20 - 100 ppm fluoride range. Pod formation was inhibited at 100 ppm fluoride amended soil in case of Mung, and 50 ppm in Ladies finger, 40 - 100 ppm in Maize and 30 - 50 ppm fluoride amended soil in case of Chilli. Thus, Maize and Chilli are more sensitive to fluoride contamination than other crops. In all the crops NPP decreased with increase in fluoride content in soil with significant decrease in highest concentration of fluoride.

Keywords

Fluoride, Uptake, Crops, Net Primary Productivity

*Corresponding author.

How to cite this paper: Mishra, P.C., Sahu, S.K., Bhoi, A.K. and Mohapatra, S.C. (2014) Fluoride Uptake and Net Primary Productivity of Selected Crops. *Open Journal of Soil Science*, **4**, 388-398. http://dx.doi.org/10.4236/ojss.2014.411039

1. Introduction

Fluorine (F) is an element of the halogen family and Fluoride (F^-) is the anion the reduced form of fluorine. Both organic and inorganic fluorine compounds are sometimes called fluorides. Fluoride, like other halides, is a monovalent ion (−1 charge). Its compounds often have properties that are distinctly relative to other halides. Structurally, and to some extent chemically, the fluoride ion resembles the hydroxides ion. Fluoride-containing compounds range from potent toxins such as Sarin to life-saving pharmaceuticals such as Efavirenz and from refractory materials such as calcium fluoride to the highly reactive sulfur tetrafluoride. The range of fluorine-containing compounds is considerable as fluorine is capable of forming compounds with all the elements except for helium and neon [1]. Fluorine in the environment is therefore found as fluorides which together represent about 0.06 - 0.09 percent of the earth's crust. The average crustal abundance is 300 $mg \cdot kg^{-1}$ [2]. Fluorides are found at significant levels in a wide variety of minerals, including fluorspar, rock phosphate, cryolite, apatite, mica, hornblende and others [3]. Fluorite (CaF_2) is a common fluoride mineral of low solubility occurring in both igneous and sedimentary rocks. Fluoride is commonly associated with volcanic activity and fumarolic gases. Thermal waters, especially those of high pH, are also rich in fluoride [4]. Minerals of commercial importance include cryolite and rock phosphates. The fluoride salt cryolite is used for the production of aluminium [3] and as a pesticide [5]. Rock phosphates are converted into phosphate fertilizers by the removal up to 4.2 percent fluoride. The purified fluoride (as fluorosilicates) is added to drinking-water in some countries in order to protect against dental caries [6] and [7]. It forms inorganic and organic compounds called fluorides. Living organisms are mainly exposed to inorganic fluorides through food and water. Based on quantities released and concentrations presented naturally in the environment as well as the effects on living organisms, the important inorganic fluorides are hydrogen fluoride (HF), calcium fluoride (CaF_2), sodium fluoride (NaF), Sulphur hexafluoride (SF_6) and Silico fluorides. Fluoride in the form of HF or SiF_4 is one of the most important and damaging air pollutants affecting forests, crops and natural vegetation [8]. Fluoride occurs naturally in plants, but its presence has attracted attention primarily in certain areas where concentrations are elevated above normal by accumulation from the atmosphere.

Human activities releasing fluorides into the environment are mainly the mining and processing of phosphate rock and its use as agricultural fertilizer, as well as the manufacture of aluminums. Other fluoride sources include the combustion of coal (containing fluoride impurities) and other manufacturing processes (steel, copper, nickel, glass, brick, ceramic, glues and adhesives). In addition, the use of fluoride-containing pesticides in agriculture and fluoride in drinking water supplies also contribute to the release of fluorides into the environment. However, the greatest concentrations are found near anthropogenic point sources. In air, because of its extensive industrial use, hydrogen fluoride is probably the greatest single atmospheric fluoride contaminant [9]. Fluorides can be present as gases or particulates. They can be transported by wind over large distances before depositing on the earth's surface or dissolving in water. In general, fluoride compounds do not remain in the troposphere for long periods, nor do they move up to the stratosphere. In areas where fluoride-containing coal is burned or phosphate fertilizers are produced or used, the fluoride concentration in air is elevated leading to increased exposure by inhalation and absorption routes. High levels of atmospheric fluoride occur in areas of Morocco and China [10] and [11]. In some provinces of China, fluoride concentrations in indoor air ranging from 16 to 46 $\mu g/m^3$ owing to indoor combustion of high-fluoride coal for cooking, or drying and curing food [12]. Indeed, more than 10 million people in China are reported to suffer from fluorosis, related in part to the burning of high fluoride coal [13].

Fluoride is a component of most types of soil, with total concentrations ranging from 20 to 1000 µg/g in areas without natural phosphate or fluoride deposits and up to several thousand mg/g in mineral soils with deposits of fluoride [14]. Airborne gaseous and particulate fluorides tend to accumulate within the surface layer of soils, but they may be displaced throughout the root zone, even in calcareous soils [15]. Calcium fluoride is the most common in alkaline soils, and fluoroaluminate complexes are the most common in acidic soils. Thus, exposure to hydrofluoric acid will occur at a hazardous waste site only if someone comes in to contact with material leaking from a storage container or contaminated air before it is dispersed. Once in a stable form, fluoride persists in the environment for a relatively long time unless transforming to another compound or decomposed by radiation. The clay and organic carbon content as well as the pH of soil is primarily responsible for the origin and/or retention of fluoride in soils. It has also been reported that in saline soils the bioavailability of fluoride to plants is related to the water-soluble component of the fluoride present [14]. In living organisms, the quantity of fluoride accumulation depends on the route of exposure, on how well the particular fluorides are absorbed by the body and on how quickly they are taken up and excreted. Soluble fluorides are bioaccumulated by some aquatic and terrestrial biota. However, information concerning the biomagnification of fluoride in aquatic or terrestrial food-chains is scanty [16] and [17]. Inorganic fluorides tend to accumulate preferentially in the skeletal and dental hard tissues of vertebrates, exoskeletons of invertebrates and cell walls of plants [14] [16] [18]-[20]. Bio-concentration factors greater than 10 (expressed on a wet weight basis) were reported in both aquatic plants and animals following exposure to solutions up to 50 mg/l of fluoride [21]. Moeri [22] has reported effect of fluoride emission on enzyme activity in metabolism of plants.

The undivided Sambalpur District of Odisha is an industrial belt where two aluminium industries—Vedanta Aluminum Company at Jharsuguda and Hindalco Industries Limited at Hirakud Town have been established. The former started operating from 1965 while Vedanta, a major industry, is operating since last 8 years. Both the industries have their coal-based captive thermal power plants. The local people in Hirakud complain every year of crop damage during growing season due to emissions from aluminium and power industries in Hirakud. There are research reports on fluoride accumulation in soil, plants and animals to the extent of 40 - 80 ppm in Hirakud, which may be because of emissions from industrial activities [23] [24]. Effects of such accumulations on various environmental segments in Hirakud have also been studied [25] [26]. A survey of field soil around Vedanta Aluminium Limited shows a total and leachable fluoride content ranging from 94.01 - 467.7 mg/kg and 10.60 - 104.86 mg/kg respectively [27]. Therefore, the present study was undertaken to assess the fluoride uptake by selected crops and its effect on NPP.

2. Materials and Methods

Sodium fluoride (NaF) was used to prepare fluoride (F) solutions in various concentrations, *i.e*. 20, 40, 60, 80, and 100 ppm with distilled water for treatment. Tap water was used as control. Culture experiments were set up to monitor the growth of the plants in various concentrations of F^- amended soil. Plant seeds were collected from a Government authorized seed store located at Goshala, Sambalpur and the seedlings were collected from OUAT Chipilima, Sambalpur for pot culture. For pot culture experiment, 21 days old healthy seedlings were collected from OUAT, Chiplima and transplanted in to the pots containing F^- treated crop field soil. After harvest total yield (NPP) was calculated. Following local crops were assessed:

Winter crops—Brinjal (*Solanum melongena* L.), Tomato (*Lycopersicon esculentum*), Mustard (*Brassica compestris*) and Mung (*Vigna radiata*);

Summer crops—Ladies finger (*Abelmoschus esculentus*) and Maize (*Zea mays* L.);

Rainy crops—Paddy (*Oryza sativa*) and Chilli (*Capsicum annuum*).

NPP is usually estimated by harvest technique, in which above ground plant biomass (AGP) is harvested from all the pots and below ground Plant Biomass (BGP) were washed from soil cores. The short term harvest method [28] was employed for biomass estimation at 15 days intervals. The plant parts were oven dried at 80˚C for 24 hours. After harvest total yield was calculated. The F^- content in soil and plants was estimated by Ion Selective Analyzer.

3. Results

3.1. Brinjal

The total and leachable F^- content in soil at the beginning of the experiment was found to be 95.19 and 8.89 ppm respectively. The F^- content in plant sample after harvest was found to be 1.45, 1.89, 2.12, 2.85, 3.24 and 3.83 mg/kg in 0, 20, 40, 60, 80 and 100 ppm of F treated soils (**Table 1**). NPP on the day of harvest (*i.e.* 75th day) was 117.4, 109.6, 89.6, 69.1, 60.3 and 50.8 g dry wt/plant in 0, 20, 40, 60, 80 and 100 ppm F^- amended soils respectively (**Table 2**). Compared to control, NPP was decreased by 6.64% and 56.72% in 20 and 100 ppm of F^- concentrations respectively. The yield (pod weight) decreased by 78% at 100 ppm F^- application compared to control.

3.2. Tomato

The total and leachable $\mathbf{F^-}$ content in soil at the beginning was 95.19 and 8.89 ppm respectively. At the time of harvest *i.e.* on 75th day, the total F^- content showed decreasing trend whereas leachable F^- showed an increasing trend in both control and treated soil (**Table 3**). The F^- content in plant sample after harvest was found to be

Table 1. Fluoride content in soil and Brinjal plant.

Conc.	At Start in Soil (mg/Kg)		At Harvest (mg/Kg)		
	Total Fluoride	Leachable Fluoride	Total Fluoride in Soil	Leachable Fluoride in Soil	Total F^- in Plant Sample
Control	95.19	8.89	86.40	18.56	1.45
20 ppm	95.19 + 20	8.89	92.40	21.58	1.89
40 ppm	95.19 + 40	8.89	110.20	25.63	2.12
60 ppm	95.19 + 60	8.89	124.60	29.76	2.85
80 ppm	95.19 + 80	8.89	138.50	35.80	3.24
100 ppm	95.19 + 100	8.89	158.40	38.14	3.83

Table 2. NPP (g dry wt/plant) in Brinjal in fluoride treated soil.

Days	Concentration	BGP Root	AGP			NPP (BGP + AGP)	% Decrease in NPP over control
			Leaf	Stem	Pod		
	60 Days Control	7.1	16.6	32.2	61.5	117.4	00
	20 ppm	6.8	15.8	29.7	57.3	109.6	6.64
	40 ppm	6.2	15.1	27.2	41.1	89.6	23.67
	60 ppm	5.9	13.7	24.2	25.3	69.1	41.14
	80 ppm	5.1	12.1	23.5	19.6	60.3	48.63
	100 ppm	4.2	11.5	21.6	13.5	50.8	56.72

Table 3. Fluoride content in soils of Tomato crop.

Soil →	At the Start (mg/Kg)		During Harvest (mg/Kg)		
Conc.	Total Fluoride	Leachable Fluoride	Total Fluoride in Soil	Leachable Fluoride in Soil	Total F^- in Plant Sample
Control	95.19	8.89	86.40	22.87	1.05
20 ppm	95.19 + 20	8.89	92.40	23.70	1.66
40 ppm	95.19 + 40	8.89	110.20	27.52	2.08
60 ppm	95.19 + 60	8.89	124.60	31.47	2.68
80 ppm	95.19 + 80	8.89	138.50	33.30	3.17
100 ppm	95.19 + 100	8.89	158.40	37.28	3.49

1.05, 1.66, 2.08, 2.68, 3.17 and 3.49 mg/kg in 0, 20, 40, 60, 80 and 100 ppm of F^- amended soils respectively.

NPP on the day of harvest (*i.e.* 60th day) was 116.0, 99.2, 69.3, 65.2, 54.4 and 43.8 g dry wt/plant in 0, 20, 40, 60, 80 and 100 ppm F^- amended soils respectively (**Table 4**). NPP decreased by 14.48% - 62.24% in 20 - 100 ppm F^- amended soils compared to control set. The pod weight decreased by 83% in 1000 ppm F^- treated soils over control.

3.3. Mustard

The total and leachable F^- content in soil in the beginning was 95.19 and 8.89 ppm respectively. At the time of harvest *i.e.* on 60th day, the total F^- content decreased whereas leachable F^- increased both in control and treated soils (**Table 5**). The F^- content in plant sample on harvest was found to be 1.13, 1.46, 1.76, 1.95, 2.18 and 2.37 mg/kg in control, 10, 20, 30, 40 and 50 ppm of F^- treated soils respectively.

On 60th day, the highest NPP (0.263 g dry wt/plant) was recorded in case of control set and least (0.102 g dry wt/plant) in 50 ppm F^- treated soil. The percentage decrease in NPP on 60th day was found to be 15.58, 27.37, 49.04, 58.93 and 61.21% in 10, 20, 30, 40 and 50 ppm F^- treated soils respectively (**Table 6**) whereas Mustard yield got reduced by 62% in 50 ppm F^- treated soil.

Table 4. NPP (g dry wt/plant) of Tomato in fluoride treated soils.

Days	Concentration	BGP Root	AGP			NPP (BGP + AGP)	% Decrease in NPP over Control
			Leaf	Stem	Pod		
60 Days	Control	6.3	20.0	31.3	58.4	116.0	00
	20 ppm	5.0	18.6	28.0	47.6	99.2	14.48
	40 ppm	4.8	16.4	26.2	39.9	69.3	40.25
	60 ppm	4.3	14.3	24.1	22.5	65.2	43.79
	80 ppm	3.1	13.7	22.8	14.8	54.4	53.10
	100 ppm	2.2	11.5	20.4	9.7	43.8	62.24

Table 5. Fluoride content in soils and Mustard plant.

Soil →	At the Start (mg/Kg)		During Harvest (mg/Kg)		
Conc.	Total Fluoride	Leachable Fluoride	Total Fluoride in Soil	Leachable Fluoride in Soil	Total F^- in Plant Sample
Control	95.19	8.89	81.38	16.37	1.13
10 ppm	95.19 + 10	8.89	87.70	18.95	1.46
20 ppm	95.19 + 20	8.89	93.37	22.61	1.76
30 ppm	95.19 + 30	8.89	99.61	26.57	1.95
40 ppm	95.19 + 40	8.89	106.72	30.59	2.18
50 ppm	95.19 + 50	8.89	112.58	32.18	2.37

Table 6. NPP (g dry wt/plant) of Mustard in fluoride treated soils.

Days	Concentration	BGP Root	AGP			NPP (BGP + AGP)	% Decrease in NPP over Control
			Leaf	Stem	Pod		
60 Days	Control	0.034	0.046	0.091	0.092	0.263	0
	10 ppm	0.033	0.043	0.07	0.076	0.222	15.58
	20 ppm	0.03	0.035	0.063	0.063	0.191	27.37
	30 ppm	0.024	0.031	0.054	0.025	0.134	49.04
	40 ppm	0.022	0.026	0.043	0.017	0.108	58.93
	50 ppm	0.021	0.021	0.036	0.014	0.102	61.21

3.4. Mung

The total and leachable F^- content in soil in the beginning was 95.19 and 8.89 ppm respectively. At the time of harvest *i.e.* on 60th day, the total F^- content decreased whereas leachable F^- increased both in control and treated soils (**Table 7**). The F^- content in plant sample after harvest was found to be 1.23, 1.72, 2.18, 2.76, 3.35 and 3.63 mg/kg in control, 10, 20, 30, 40 and 50 ppm of F^- treated soils respectively.

NPP on the harvest day was 36, 32.3, 28.8, 26.9, 25.0 & 16.7 g of dry wt/plant in control, 20, 40, 60, 80 and 100 ppm F^- treated soils respectively (**Table 8**). In comparison with control, NPP decreased by 10.27%, 20%, 25.27%, 30.55% and 53.61% in 20, 40, 60, 80 and 100 ppm F^- amended sets respectively. Mung yield decreased by 14% at 80 ppm F^- treatment and no pod formation took place at 100 ppm F^- concentration.

3.5. Ladies Finger

On harvest day *i.e.* 60th day, the total F^- content decreased and leachable F^- increased both in control and treated soils (**Table 9**). The total and leachable F^- content in soil in the beginning of the experiment was 95.19 and 8.89 ppm respectively. The F^- content in ladies finger plants during harvest was found to be 1.44, 1.55, 1.86, 2.03, 2.35 and 2.72 mg/kg in control, 10, 20, 30, 40 and 50 ppm of F^- treated soils respectively.

On the day of harvest (*i.e.* 60th day), NPP was found to be 87.9, 77.1, 69.9, 64.6, 60.8 and 41.5 g of dry

Table 7. Fluoride content in soils and Mung plants.

Soil → Conc.	At the Start (mg/Kg)		During Harvest (mg/Kg)		
	Total Fluoride	Leachable Fluoride	Total Fluoride in Soil	Leachable Fluoride in Soil	Total F^- in Plant Sample
Control	95.19	8.89	86.40	22.93	1.23
20 ppm	95.19 + 20	8.89	92.40	24.52	1.72
40 ppm	95.19 + 40	8.89	110.20	29.25	2.18
60 ppm	95.19 + 60	8.89	124.60	33.07	2.76
80 ppm	95.19 + 80	8.89	138.50	36.76	3.35
100 ppm	95.19 + 100	8.89	158.40	42.04	3.63

Table 8. NPP (g dry wt/plant) of Mung in fluoride treated soils.

Days	Concentration	BGP Root	AGP			NPP (BGP + AGP)	% Decrease in NPP over control
			Leaf	Stem	Pod		
60 Days	Control	2.5	8.6	14.7	10.2	36.0	00
	20 ppm	2.2	7.4	13.6	10.2	32.3	10.27
	40 ppm	1.9	7.0	10.0	9.9	28.8	20
	60 ppm	1.6	6.4	10.0	8.9	26.9	25.27
	80 ppm	1.1	6.0	10.1	8.8	25.0	30.55
	100 ppm	1.0	5.8	9.9	---	16.7	53.61

Table 9. Fluoride content in soils and ladies finger plants.

Soil → Conc.	At the Start (mg/Kg)		During Harvest (mg/Kg)		
	Total Fluoride	Leachable Fluoride	Total Fluoride in Soil	Leachable Fluoride in Soil	Total F^- in Plant Sample
Control	95.19	8.89	81.38	17.89	1.44
10 ppm	95.19 + 10	8.89	87.70	19.24	1.55
20 ppm	95.19 + 20	8.89	93.37	23.56	1.86
30 ppm	95.19 + 30	8.89	99.61	28.67	2.03
40 ppm	95.19 + 40	8.89	106.72	32.46	2.35
50 ppm	95.19 + 50	8.89	112.58	35.04	2.72

wt/plant in control, 10, 20, 30, 40 and 50 ppm F^- treated soils respectively (**Table 10**). NPP decreased by 12.28% - 52.78% in 10 - 50 ppm F^- treated soils. There was no pod found at 50 ppm F^- treatment.

3.6. Maize

On the harvest day (75th day), the total F^- content decreased and leachable F^- increased both in control and treated soils (**Table 11**). The total and leachable F^- content in soils in the beginning of the experiment was 95.19 and 8.89 ppm respectively. In maize samples F^- was found to be 1.98, 2.46, 2.65, 3.22, 3.54 and 4.02 mg/kg in control, 20, 40, 60, 80 and 100 ppm of F^- treated soils respectively on the harvest day.

NPP on 75th day was 11.42 g of dry wt/plant in control and 4.43 g in 100 ppm F^- amended soils. The decrease in NPP was found to be 12.17%, 36.66%, 40.45%, 52.62% and 61.20% in 20, 40, 60, 80 and 100 ppm F^- treated sets respectively (**Table 12**). No pod formation was found in sets beyond 20 ppm treatment.

3.7. Paddy

On the harvest day, the total and leachable F^- content in soil at the start of the experiment was 95.19 and 8.89 ppm respectively. The F^- content in plant sample on harvest was found to be 2.16, 2.63, 2.95, 3.62, 3.84 and 4.37 mg/kg in control, 20, 40, 60, 80 and 100 ppm of F^- treated soils respectively (**Table 13**).

Table 10. NPP (g dry wt/plant) of Ladies finger in fluoride treated soils.

Days	Concentration	BGP Root	AGP			NPP (BGP + AGP)	% Decrease in NPP over Control
			Leaf	Stem	Pod		
60 Days	Control	7.8	10.0	39.3	30.1	87.9	00
	10 ppm	7.7	9.6	23.0	29.8	77.1	12.28
	20 ppm	6.3	9.4	25.1	29.1	69.9	20.47
	30 ppm	5.9	9.2	20.8	28.7	64.6	26.50
	40 ppm	4.3	8.7	20.8	27.0	60.8	30.83
	50 ppm	4.1	8.5	28.9	---	41.5	52.78

Table 11. Fluoride content in soils and Maize plants.

Soil →	At the Start (mg/Kg)		During Harvest (mg/Kg)		
Conc.	Total Fluoride	Leachable Fluoride	Total Fluoride in Soil	Leachable Fluoride in Soil	Total F^- in Plant Sample
Control	95.19	8.89	86.40	20.90	1.98
20 ppm	95.19 + 20	8.89	92.40	22.52	2.46
40 ppm	95.19 + 40	8.89	110.20	26.85	2.65
60 ppm	95.19 + 60	8.89	124.60	29.82	3.22
80 ppm	95.19 + 80	8.89	138.50	35.57	3.54
100 ppm	95.19 + 100	8.89	158.40	41.02	4.02

Table 12. NPP (g dry wt/plant) of Maize in F^- treated soils.

Days	Concentration	BGP Root	AGP			NPP (BGP + AGP)	% Decrease in NPP over Control
			Leaf	Stem	Pod		
75 days	Control	2.63	0.78	5.73	2.28	11.42	0
	20 ppm	2.46	0.74	5.33	1.5	10.03	12.17
	40 ppm	1.95	0.663	4.62	xxx	7.233	36.66
	60 ppm	1.89	0.62	4.29	xxx	6.8	40.45
	80 ppm	1.81	0.6	3.0	xxx	5.41	52.62
	100 ppm	1.4	0.55	2.48	xxx	4.43	61.20

Table 13. Fluoride content in soils and Paddy samples.

Soil →	At the Start (mg/Kg)		During Harvest (mg/Kg)		
Conc.	Total Fluoride	Leachable Fluoride	Total Fluoride in Soil	Leachable Fluoride in Soil	Total F^- in Plant Sample
Control	95.19	8.89	86.40	21.87	2.16
20 ppm	95.19 + 20	8.89	92.40	23.45	2.63
40 ppm	95.19 + 40	8.89	110.20	29.40	2.95
60 ppm	95.19 + 60	8.89	124.60	32.52	3.62
80 ppm	95.19 + 80	8.89	138.50	35.73	3.84
100 ppm	95.19 + 100	8.89	158.40	41.13	4.37

On the day of harvest (*i.e.* 75th day), the NPP of Paddy was 105.9, 97.2, 84.9, 72.1, 65.8 and 56.6 g dry wt/plant in 0, 20, 40, 60, 80 and 100 ppm F^- treated soil (Table 14). Compared with control, the NPP decreased by 8.2% - 46.5% and yield by 9.5 - 55.5 in 20 - 100 ppm F^- treated soils respectively.

3.8. Chilli

The total and leachable F^- content in soils in the beginning was 95.19 and 8.89 ppm respectively. On the harvest day *i.e.* on 75th day, the total F^- content decreased and leachable F^- increased both in control and experimental soils (**Table 15**).

F^- content in plant samples on harvest was found to be 1.56, 1.76, 1.98, 2.35, 2.58 and 2.94 mg/kg in control, 10, 20, 30, 40 and 50 ppm of fluoride treated soils respectively. NPP on the day of harvest (*i.e.* 75th day) was 7.56, 4.47, 2.77, 1.74, 1.06 and 0.71 g of dry wt/plant in 0, 10, 20, 30, 40 and 50 ppm F^- treated soils (**Table 16**). Thus NPP decreased by 40.8% - 90.65% in 20 - 100 ppm in F^- treated sets. No pod formation was seen beyond 20 ppm treatment.

Table 17 presents a comparative figure on plant uptake of fluoride and respective NPP and yield in the crops tested. Mung, Ladies finger, Maize and Chilli had no pod yield at the highest concentration of F^-, indicating that they are very sensitive plants compared to other four crops. **Figure 1** shows a comparative picture of percent reduction of NPP and yield.

Figure 1 presents a comparative figure on the rate of NPP and yield reduction at the highest concentration of F tested. All such crops are sensitive to F with Mung, Ladies finger, Maize and Chilli being far more sensitive than other four.

Table 14. NPP (g dry wt/plant) of Paddy in F^- treated soils.

Days	Concentration	BGP Root	AGP Leaf	AGP Stem	AGP Pod	NPP (BGP + AGP)	% Decrease in NPP over Control
	60 Days Control	7.9	21.0	25.3	51.7	105.9	00
	20 ppm	6.8	20.6	23.0	46.8	97.2	6.64
	40 ppm	6.1	18.4	21.1	39.3	84.9	23.67
	60 ppm	5.7	16.1	18.7	31.6	72.1	41.14
	80 ppm	5.1	14.2	16.8	29.7	65.8	48.63
	100 ppm	4.7	13.5	14.9	23.5	56.6	56.72

Table 15. Fluoride content in soils and Chilli plants.

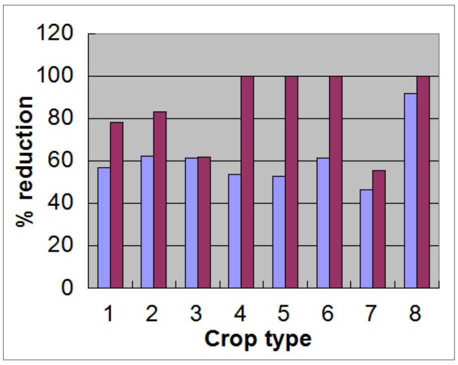
Soil →	At the Start (mg/Kg)		During Harvest (mg/Kg)		
Conc.	Total Fluoride	Leachable Fluoride	Total Fluoride in Soil	Leachable Fluoride in Soil	Total F^- in Plant Sample
Control	95.19	8.89	81.38	12.50	1.56
10 ppm	95.19 + 10	8.89	87.70	16.72	1.76
20 ppm	95.19 + 20	8.89	93.37	21.47	1.98
30 ppm	95.19 + 30	8.89	99.61	25.45	2.35
40 ppm	95.19 + 40	8.89	106.72	28.56	2.58
50 ppm	95.19 + 50	8.89	112.58	33.70	2.94

Table 16. NPP (g dry wt/plant) of Chilli in F^- treated soils.

Days	Concentration	BGP Root	AGP Leaf	AGP Stem	AGP Pod	NPP (BGP + AGP)	% Decrease in NPP over Control
75 days	Control	1.22	0.89	2.95	2.5	7.56	0
	10 ppm	1.03	0.8	2.06	0.56	4.47	40.8
	20 ppm	0.87	0.8	1.68	0.42	2.773	63.32
	30 ppm	0.42	0.38	0.93	xxx	1.74	76.9
	40 ppm	0.30	0.37	0.39	xxx	1.06	85.9
	50 ppm	0.26	0.24	0.21	xxx	0.71	90.65

Table 17. Leachable Fluoride (ppm) content, NPP and yield (g dry wt/plant) of Crops in highest concentration of F^-.

Crop	F Conc.	Soil F	Plant F	NPP	Yield
Brinjal	100	38.14	3.83	50.8	13.5
Tomato	100	37.28	3.49	43.8	9.7
Mustard	50	32.18	2.37	0.102	0.014
Mung	100	42.04	3.63	16.7	Nil
Ladies Finger	50	35.04	2.72	41.5	Nil
Maize	100	41.02	4.02	4.43	Nil
Paddy	100	41.13	4.37	56.6	23.5
Chilli	50	33.7	2.94	0.71	Nil



(1: Brinjal; 2: Tomato; 3: Mustard; 4: Mung; 5: Ladies finger; 6: Maize; 7: Paddy; 8: Chilli.)

Figure 1. Percent reduction in NPP and yield in crops.

4. Discussion

Terrestrial plants may accumulate inorganic fluorides following airborne deposition and uptake from the soil [14]. Sloof *et al*. [21] reported that the main route of uptake of fluoride by plants was from aerial deposition on the plant surface. Plant uptake from soil is generally low (except for accumulators) unless the fluoride has been added suddenly, such as following amendment with sludge or phosphate fertilizer. The availability of plants tends to decrease with time following application of fluoride. The degree of accumulation depends on several factors, including soil type and most prominently pH. At acidic pH (below pH 5.5), fluoride becomes more phyto-available through complexation with soluble aluminium fluoride species, which are themselves taken up by plants or increase the potential for the fluoride ion to be taken up by the plant [29] (Stevens *et al*. (1997)). Plant uptake of fluoride from solution culture is dependent on plant species and positively related to the ionic strength of the growth solution. Once a threshold fluoride ion activity in nutrient solutions is reached, fluoride concentrations in plants increase rapidly [30]. Ample evidences are also available relating to fluoride accumulation in different parts of the plants [31]. When fluoride contaminated plant tissue is ingested by the animals including human beings, fluoride associated problems are encountered. In the present study the same thing is also observed. Maximum fluoride accumulation in plant tissue was found in higher concentration of fluoride treated soils. Among all soils, it is the soluble fluoride content that is biologically important to plants and animals. It has also been reported that in saline soils, the bioavailability of fluoride of plants is related to the water-soluble component of the fluoride present [14]. Hocking *et al*. [32] indicated that although there was some accumulation of inorganic fluoride in marine vegetation, the rate of accumulation was far lower than that of airborne inorganic fluoride by terrestrial plants. Fluoride (F^-) contamination of soil, water and vegetation has been a continuing problem in the world. Various sources of F^- and their impact on the biology of plants and animals have been well documented. The detrimental effects of F^- on plants and animals have been known for more than hundred years [8]. Agricultural soils high in fluoride are common due to long term accumulation of fluoride from multisources. It may be extensive application of phosphate fertilizers, leaching from fluoride deposited rocks or industrial activities. Overall, the present study shows varied tolerance towards fluoride in the plant species tested and provides information about how fluoride can affect their germination, biochemistry and growth. Such knowledge is potentially useful for farmers to help them avoid excessive application of F^- containing fertilizers and selection of crops. As the fluoride endemicity is a great problem in recent days, much more studies on fluoride toxicity are needed not only to explore some viable remedial measures but also to save the present and future generations form fluoride related hazards. The study reveals that among the vegetable crops tested Chilli is more sensitive to fluoride contamination whereas Brinjal shows less sensitivity. Similarly, in case of grain crops (*i.e.* Maize and Rice) Maize shows more sensitivity to fluoride contamination as compared with Paddy.

The present work also indicates that the biomass of plants (both Mustard and Maize) grown in fluoride amended soil is less as compared with the control soil. This may be due to changes in above biochemical parameters which in consequence retard the growth and biomass of plants. Fluoride concentration more than 28 ppm significantly decreases dry weight of shoots [30], thus significantly reducing leaf surface area and weight in mature and immature leaves resulting in the inhibition of growth. This may be the reason for decrease in RGI with increase in fluoride concentration. Black [33] has reported that Fluoride in mesophyll cells disturbs mineral metabolism, reduces chlorophyll pigments and alters other morphological and physiological parameters such as height, number of leaves, biomass productivity, fruiting and yield of the plant, while higher fluoride accumulation causes leaf damage [31] and thus may retard growth.

References

[1] Greenwood, Norman, N. and Earnshaw, A. (1997) Chemistry of the Elements. 2nd Edition, Butterworth-Heinemann, Oxford, 1340 p.

[2] Tebutt, T.H.Y. (1983) Relationship between Natural Water Quality and Health. United Nations Educational, Scientific and Cultural Organization, Paris.

[3] Murray, J.J. (1986) Appropriate Use of Fluorides for Human Health. World Health Organization, Geneva.

[4] Edmunds, W.M. and Smedley, P.L. (1996) Groundwater Geochemistry and Health: An Overview. In: Appleton, Fuge and McCall, Eds., *Environmental Geochemistry and Health*, Vol. 113, Geological Society Special Publication, London, 91-105.

[5] USEPA (1996) R.E.D. FACTS, Cryolite, EPA-738-F-96-016. United States Environmental Protection Agency.

[6] Reeves, T.G. (1986) Water Fluoridation: A Manual for Engineers and Technicians. United States Department of Health and Human Services, Centres for Disease Control and Prevention, 138 p.

[7] Reeves, T.G. (1994) Water Fluoridation. A Manual for Water Plant Operators. United States Department of Health and Human Services, Center for Disease Control and Prevention, 99 p.

[8] Weinstein, L.H. and Davison, A.W. (2004) Fluorides in the Environment. CABI Publishing, Wallingford.

[9] WHO (1984) Guidelines for Drinking Water Equality. World Health Organisation, Geneva, 2-249.

[10] Haikel, Y. (1986) Fluoride Content of Water, Dust, Soils and Cereals in the Endemic Dental Fluorosis Area of Khouribga (Morocco). *Archives of Oral Biology*, **31**, 279-286. http://dx.doi.org/10.1016/0003-9969(86)90041-5

[11] Haikel, Y. (1989) The Effects of Airborne Fluorides on Oral Conditions in Morocco. *Journal of Dental Research*, **68**, 1238-1241.

[12] WHO (1996) Volume 2: Health Criteria and Other Supporting Information. In: *Guidelines for Drinking-Water Quality*, 2nd Edition, World Health Organization, Geneva.

[13] Gu, S.L., Rongli, J. and Shouren, C. (1990) The Physical and Chemical Characteristics of Particles in Indoor Air Where High Fluoride Coal Burning Takes Place. *Biomedical and Environmental Sciences*, **3**, 384-390.

[14] Davison, A. (1983) Uptake, Transport and Accumulation of Soil and Airborne Fluorides by Vegetation. In: Shupe, J., Peterson, H. and Leone, N., Eds., *Fluorides*: *Effects on Vegetation*, *Animals and Humans*, Paragon Press, Salt Lake City, 61-82.

[15] Polomski, J., Fluhler, H. and Blaser, P. (1982) Accumulation of Airborne Fluoride in Soils. *Journal of Environmental Quality*, **11**, 457-461.

[16] Hemens, J. and Warwick, R.J. (1972) The Effects of Fluoride on Estuarine Organisms. *Water Research*, **6**, 1301-1308.

[17] ATSDR (1993) Toxicological Profile for Fluorides, Hydrogen Fluoride, and Fluorine. US Department of Health and Human Services, Agency for Toxic Substances and Disease Registry (TP-91/17), Atlanta.

[18] Michel, J., Suttie, J. and Sunde, M. (1984) Fluorine Deposition in Bone as Related to Physiological State. *Poultry*

Science, **63**, 1407-1411.

[19] Kierdorf, H. and Kierdorf, U. (1997) Disturbances of the Secretory Stage of Amelogenesis in Fluorosed Deer Teeth: A Scanning Electron-Microscopic Study. *Cell and Tissue Research*, **289**, 125-135.

[20] Sands, M., Nicol, S. and McMinn, A. (1998) Fluoride in Antarctic Marine Crustaceans. *Marine Biology*, **132**, 591-598.

[21] Sloof, W., Eerens, H., Janus, J. and Ros, J. (1989) Integrated Criteria Document: Fluorides. Bilthoven, National Institute of Public Health and Environmental Protection (Report No. 758474010).

[22] Moeri, P.B. (1980) Effect of Fluoride Emission in Enzyme Activity in Metabolism of Agric Plants. *Fluoride*, **13**, 122-128.

[23] Rath, S.P., Sarangi, P.K. and Mishra, P.C. (1998) Bioaccumulation and Bioconcentration of Fluoride in Environmental Segments of Hirakud, India. *Indian Journal of Environmental Protection*, **18**, 199-202.

[24] Mishra, P.C., Pradhan, K., Meher, K. and Bhosagar, D. (2009) Fluoride in the Environmental Segments at Hirakud of Western Orissa, India. *African Journal of Environmental Science and Technology*, **3**, 260-264.

[25] Mishra, P.C. and Mohapatra, A.K. (1998) Haematological Characteristics and Bone Fluoride Content in *Bufo melanostictus* from an Aluminium Industrial Site. *Environmental Pollution*, **99**, 421-423.

[26] Mishra, P.C. and Pradhan, K. (2006) Prevalence of Fluorosis among School Children and Cattle Population in Hirakud Town of Orissa. *Bioscan*, **2**, 31-36.

[27] Mishra, P.C. and Sahu, S.K. (2013) Effect of Fluoride on Locally Available Crops. Project Report Submitted to Vedanta Aluminium Company Ltd., Jharsuguda, 124 p.

[28] Odum, E.P. (1960) Organic Production and Turnover in Old Field Succession. *Ecology*, **41**, 34-49.

[29] Stevens, D.P., McLaughlin, M.J. and Alston, A.M. (1997) Phytotoxicity of Aluminium-Fluoride Complexes Culture by *Avena sativa* and *Lycopersicon esclentum*. *Plant and Soil*, **192**, 81-93.

[30] Stevens, D.P., McLaughlin, M.J. and Alston, A.M. (1998) Phytotoxicity of Hydrogen Fluoride and Fluoroborate and Their Uptake from Solution Culture by *Lycopersicon esculentum* and *Avena sativa*. *Plant and Soil*, **200**, 175-184.

[31] Klumpp, A., Klump, G., Domingos, M. and Silva, M.D.D. (1996) Fluoride Impact on Native Tree Species of the Atlantic Forest near Cubatao, Brazil. *Water*, *Air and Soil Pollution*, **87**, 57-71. http://dx.doi.org/10.1007/BF00696829

[32] Hocking, M.B., Hocking, D. and Smyth, T.A. (1980) Fluoride Distribution and Dispersion Processes about an Industrial Point Source in a Forested Coastal Zone. *Water*, *Air*, *& Soil Pollution*, **14**, 133-157.

[33] Black, C.A. (1968) Nitrogen, Phosphorus and Potassium. In: *Soil Plant Relationships*, 2nd Edition, John Wiley and Sons, New York, 405-773.