

# Assessment of Fluoride Concentration of Soil and Vegetables in Vicinity of Zinc Smelter, Debari, Udaipur, Rajasthan

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## ABSTRACT

**Background:** As of late, natural contamination has stimulated as a reaction of mechanical and other human exercises. In India, with the expanding industrialization, numerous unsafe substances are utilized or are discharged amid generation as cleans, exhaust, vapours and gasses. These substances at last are blended in the earth and causes health hazards.

**Objective:** To determine concentration of fluoride in soils and vegetables grown in the vicinity of Zinc Smelter, Debari, Udaipur, Rajasthan.

**Materials and Methods:** Samples of vegetables and soil were collected from areas situated at 0, 1, 2, 5, and 10 km distance from the zinc smelter, Debari. Three samples of vegetables (i.e.

Cabbage, Onion and Tomato) and 3 samples of soil (one sample from the upper layer of soil (i.e. 0 to 20 cm) and one from the deep layer (i.e. 20 – 40 cm)) at each distance were collected. The soil and vegetable samples were sealed in clean polythene bags and transported to the laboratory for analysis. One sample each of water and fertilizer from each distance were also collected.

**Results:** The mean fluoride concentration in the vegetables grown varied between  $0.36 \pm 0.69$  to  $0.71 \pm 0.90$  ppm. The fluoride concentration in fertilizer and water sample from various distances was found to be in the range of 1.4 – 1.5 ppm and 1.8 – 1.9 ppm respectively.

**Conclusion:** The fluoride content of soil and vegetables was found to be higher in places near to the zinc smelter.

**Keywords:** Fluoride pollution, Fluorosis, Industrial area

## INTRODUCTION

Pollution is a result of human activities resulting in impure environment. The inhalation of products of combustion, as particles and gases from fuels, has long been recognized as a cause of ill health and premature death.

Over 3 million unexpected losses worldwide have been accounted for because of urban outdoor air contamination and indoor air contamination from strong fuel. These have added to 3.2% of the worldwide weight of sickness and more than 50% of which is borne by exercises in creating nations. Unfriendly wellbeing impacts, including respiratory diseases, coronary illness and lung cancer are identified with air pollution, diminution of which would definitely reduce the global health burden related with these sicknesses [1,2]. Cengeloglu et al., proposed that fluoride contamination in the earth is customarily created by two channels; normal and anthropogenic [3]. Common fluoride wins in minerals and in geochemical stores and is by and large discharged into subsoil water sources by moderate characteristic debasement of fluorine contained in rocks (WHO) [4]. Anthropogenic fluoride contamination happens by human exercises like industrialization, motorization, utilization of fluoride containing pesticides and the fluoridation of drinking water supplies (Low and Bloom) [5]. Anthropogenic wellsprings of fluoride into the earth incorporate the modern creation and utilization of chemicals, for example, Hydrogen fluoride (HF), Calcium fluoride (CaF), Sodium fluoride (NaF), Fluorosilicic corrosive (H SiF), Sodium hexafluorosilicate (Na SiF), Sulfur hexafluoride (SF), and Phosphate manures. Phosphate composts are the significant wellspring of fluoride contamination of agricultural soils [6,7].

Fluoride, as is no doubt, an anticariogenic agent and consequently fluoridation of public water supplies to a level of around 1.0 mg dm<sup>-3</sup> is presently very common (Campbell) [8]. However, it is essential to carefully screen the levels of fluoride in light of the incidental health hazards connected with high fluoride levels in drinking water and indeed foods. The common health hazards connected with

ingestion of high fluoride incorporate mottling of the teeth, bone density deterioration, muscle spasm which harm the lungs and heart and can bring about death too. At low levels it can aggravate eyes, skin and lungs [5,9].

Fundamental constituents of air pollutants are hydrogen fluoride, sulfur dioxide, oxides of nitrogen, hostile and harmful smoke fumes, vapours, gasses and different toxins. Presently when fluoride is discharged to the air as gas or particulate it might be conveyed by the wind and saved on encompassing vegetation and soil. Subsequently, the fluoride levels in mechanical effluents should likewise be observed [5].

In India, the states of Andhra Pradesh, Bihar, Chhattisgarh, Haryana, Karnataka, Madhya Pradesh, Maharashtra, Orissa, Punjab, Rajasthan, Tamil Nadu, Uttar Pradesh and West Bengal are affected by fluoride contamination in water. Ground water fluoride contents in high levels are present in most of the districts and of Rajasthan and Andhra Pradesh. Estimation finds that 65% of India's villages are exposed to fluoride risk [9-12]. The WHO guidelines for fluoride are 1.5 mg/L if there is insufficient fluoride content within the water [13].

The environmental monitoring around the industrial settings is been done over the years by many researchers to keep an eye on the pollution created by the industries and the ill effects of the pollutants on the health of the community. It also helps in preventing the occupational hazards.

Even though, fluoride, unlike sulphur, nitrogen and chlorine, is not an essential element for plants, its background concentration is generally quite low (often as low as 1 and usually less than 10 µg F/g dry weight in most species). This is a result of the natural occurrence of F in air in close to detection limit, furthermore plants take up little F from the soil. Since the fluoride compounds like HF and SiF<sub>4</sub> are more dangerous (between 1 and 3 orders) when contrasted with different compounds (O<sub>3</sub>, SO<sub>2</sub>, PAN, Cl<sub>2</sub>, or HCl), even little arrivals of fluorides into the air can bring about extraordinary harms

to plants [5,7]. Consequently, F is most critical and damaging air pollutants influencing backwoods, yields and regular vegetation, so biomonitoring for fluoride contamination; building up fitting air quality criteria for fluoride; and deciding the measures of fluoride in air, soil, vegetation and water are basic assignments for the researchers [14,15].

Fluoride contamination of soil is fundamentally because of utilization of phosphorous fertilizers which contain less than 1 to more than 1.5% Fluorine. Its conduct in soil relies on soil pH and content of clay minerals in the soil [16]. The normal total fluoride content of soil ranges from 150-400 mg/kg. In heavy clay soils, values surpassing 1000 mg/kg have been enlisted. Polluted soil influences human wellbeing through direct contact with soil, by means of inhalation of soil contaminants which have vapourized, through ingestion of polluted sustenance items and by penetration of soil defilement into groundwater utilized for human utilization [17-20].

Thus it is imperative to evaluate the fluoride levels in soils and vegetation in regions in vicinity of facilities producing phosphorous fertilizers, steel, aluminium, zinc and ceramic industries, glass factories, and heat and power plants, which are the primary source of fluoride pollution.

The Udaipur district is endowed with metallic as well as non-metallic mineral wealth; the important are lead-zinc, copper, rock phosphate, soapstone, limestone, barytes, marble, etc.

Highly polluting activities are due to extractive metallurgical and smelting processes. Air pollutants such as hydrogen fluoride, sulfur dioxide, oxides of nitrogen etc are emitted in high quantities through some of these process. Various heavy metals: lead, arsenic, chromium, cadmium, nickel, copper, and zinc are also released by these facilities [20].

Zinc and Lead smelter is being operated at Debari, Udaipur, Rajasthan, for so many years. As hydrogen fluoride is one of the pollutants which are emitted by the smelter, so it is very important to know the fluoride level around the smelter in the Debari, Udaipur. Also not many studies have been conducted till date to estimate fluoride level around the zinc smelter, Debari. Hence, the aim of this paper is to determine concentration of fluoride in soils and vegetables grown in the vicinity of Zinc Smelter, Debari, Udaipur, Rajasthan, India.

## MATERIALS AND METHODS

### Study Area and study design

An invitro study was performed in 2014 in the areas within the 10 km radius of Zinc Smelter, Debari village, Udaipur, Rajasthan and was carried out at Department of Public Health Dentistry, Pacific Dental College and Hospital, Debari, Udaipur Rajasthan

**Ethical clearance:** Ethical clearance was obtained from the ethical committee of Pacific Dental College and Hospital, Debari, Udaipur.

**Sample Collection:** The soil and vegetable samples were collected from a randomly selected direction (south) at 0, 1, 2, 5 and 10 km distance from the zinc smelter. At each distance, randomly 3 sites were selected and from each site samples of commonly grown vegetables were collected. The vegetables sampled were Cabbage (*Brassica oleracea*), Onion (*Allium Cepa*) and Tomato (*Lycopersicon Esculentum*). Similarly from the vicinity of same sites soil samples were collected in the following manner – (1) Surface soil (0–20 cm) (2) soil from deep layer (20–40 cm). The soil and vegetable samples were sealed in clean polythene bags. At each distance water samples were collected from the major irrigation source. Water samples were collected in plastic bottles. Also sample of fertilizers used at each distance were collected in clean polythene bags. All the samples collected were transported to the laboratory for analysis.

**Sample preparation for Fluoride Determination:** Vegetables were washed and rinsed with deionized water (F- content 0 ppm)

and dried for 48 hours at 80°C. Samples were then ground and stored in clean dry, tightly closed plastic bottles. Before use these bottles were rotated to mix the sample thoroughly. These were then analysed for fluoride content using potentiometric ion selective electrode method. Fluoride was extracted from the powder with HNO<sub>3</sub> followed by aqueous KOH [21].

A F-specific ion electrode was used to determine F amounts in the solutions. These were registered in an ion analyser instrument which was calibrated with standards of known concentrations of NaF in distilled and deionized water. The supernatant was mixed 1:1 with a total ionic strength adjustment buffer (TISAB-IV) to dissociate F-Complexes and stabilize pH. The buffer is prepared by mixing 84 ml conc. HCl, 242 g TRIS (hydroxymethyl aminomethane, and 239 g sodium tartrate (FW=230.08), in about 500 mls water, cooled, and transferred to 1 liter volumetric flask and made up to mark [22].

For analysis of soil samples, the samples were air-dried and crushed, and the gravels were picked out. Fluoride content was determined after the soil samples were decomposed by fusion with NaOH in Ni crucibles, at 600°C for 30 minutes. These fused samples were then dissolved with deionized water and mixed with the TISAB buffer solution to determine F content using ion selective electrode method [23]. The water samples and fertilizers were analysed for fluoride by ion selective electrode method.

## STATISTICAL ANALYSIS

Statistical analyses were performed using one-way ANOVA and student t-test using SPSS 19 software.

## RESULTS

[Table/Fig-1] shows that mean fluoride concentration in the vegetables grown varied between 0.36 ± 0.69 to 0.71 ± 0.90 ppm with the significantly (p = 0.001) highest mean concentration of fluoride (0.71 ± 0.90 ppm) at the place nearest to the smelter (0 km). With respect to soil layers, it was observed that mean fluoride concentration was significantly highest at 0 km from smelter in upper soil layer (189 ± 1) and deeper soil layer (139 ± 1). Moreover, upper soil layer revealed significantly greater mean F concentration than deeper soil layers at all distances.

[Table/Fig-2] shows the fluoride concentration of fertilizer and water used at the different distances in the study area. The fluoride concentration in fertilizer and water sample from various distances

Distance (km)	Fconc. in vegetables (ppm) (Mean ± SD)	Fconc. in soil (ppm) (Mean ± SD)		p-value <sup>®</sup>
		Upper layer	Deeper layer	
0	0.71 ± 0.90	189 ± 1	139 ± 1	0.001*
1	0.66 ± 0.84	179 ± 1	128 ± 1	0.001*
2	0.56 ± 0.71	168.3 ± 0.58	108 ± 0	0.001*
5	0.39 ± 0.53	101.67 ± 0.58	97.33 ± 0.58	0.001*
10	0.36 ± 0.69	101.67 ± 0.58	98 ± 0	0.001*
p-value <sup>®</sup>	0.79	0.001*	0.001*	

**[Table/Fig-1]:** Comparative assessment of Fluoride concentration in vegetables and soils at various distances from Zinc Smelter

SD – Standard deviation

Test applied – # - One-way ANOVA

® - Student t-test

\*Indicates statistically significant differences

Distance (km)	Fconc. in ppm	
	Fertilizer	Water
0	1.50	1.90
1	1.40	1.90
2	1.50	1.80
5	1.50	1.80
10	1.40	1.80

**[Table/Fig-2]:** Fluoride concentration in fertilizer and water at various distances

was found to be in the range of 1.4 – 1.5 ppm and 1.8 – 1.9 ppm respectively.

## DISCUSSION

Fluoride is 13<sup>th</sup> most abundant element of the earthcrust and represents about 0.3 g/kg of earth's crust, mainly found as sodium fluoride or hydrogen fluoride which are present in minerals fluorapatite, topaz and cryolite [9]. It is common constituent of rocks and soil.

Fluorine in micro concentrations is required for healthy teeth. Excessive fluoride intake at chronic levels over long periods of time can lead to dental and skeletal fluorosis with clinical features of brown stains, surface pitting, brittleness and excessive wear, which is a significant cause of morbidity in a number of regions in the world [24].

The present study explains the mean fluoride concentration in the vegetables grown in the vicinity of smelter, which varied between  $0.36 \pm 0.69$  to  $0.71 \pm 0.90$  ppm with the significantly ( $p = 0.001$ ) highest mean concentration of fluoride ( $0.71 \pm 0.90$  ppm) at the place nearest to the smelter (0 km). These values are out of the threshold limit  $1.00 \text{ mg/kg}^3$ . These findings are fairly similar to the studies of Mezghani I et al., their study confirmed that vegetation in vicinity of the factory accumulates large quantities of F with variable specific symptoms of toxicity and according to them as expected, F concentrations decreased with increasing distance from the pollution source [7]. Brougham KM et al., suggested that the concentrations of fluoride in vegetation and soils in vicinity of aluminium smelter decreases after 36 weeks of shut down of the smelter [25].

The present study suggests that the fluoride pollution of soil is inversely related with the distance from the pollution source in each case. With respect to soil layers, it was observed that mean fluoride concentration was significantly higher in areas nearer to smelter in upper soil layer ( $189 \pm 1$ ) and deeper soil layer ( $139 \pm 1$ ). Moreover, upper soil layer revealed significantly greater mean F concentration than deeper soil layers at all distances.

Few studies conducted by Goutam R et al., and Yadav R et al., shows that there is effect of irrigating water on fluoride content of vegetables and soil [21,26]. It revealed that using fertilizer can also affect the fluoride concentration of soil thus the vegetables. In this present study we took the samples of water and fertilizer from each distance in the study area and their fluoride content was estimated. This was done to check the fluoride concentration of water and fertilizer used in the study area had any effect on fluoride concentration of vegetables and soil. The fluoride concentration in fertilizer and water sample from various distances was found to be in the range of 1.4 – 1.5 ppm and 1.8 – 1.9 ppm respectively. As the fluoride concentration of water and fertilizer was almost constant at all the distances in study area hence the effect was constant throughout the samples used for the study.

After evaluating the data of the present study it was observed that the fluoride content of soil and vegetables was found to be higher in places near to the zinc smelter and the concentration was found to be low at the places distant to the zinc smelter.

## LIMITATIONS

The study was performed under the following limitations: Bias may occur in collection of soil sample as in depth and size of sample collected. The vegetation sample collected may result in selection bias because various studies suggest that fluoride uptake by leafy vegetables is naturally higher than non-leafy ones. In the present study we have not evaluated oral and systemic manifestations due to utilization of the vegetables having higher concentrations of fluoride. Hence, there is augmentation for further studies to check the oral and systemic manifestations as a result of the same.

## CONCLUSION

Considering the above mentioned limitations, it could be concluded that most of the investigated soil samples have total fluoride levels above the maximum permissible value in agricultural soils. These soils have naturally high contents of fluorine. Highest values were found on locations nearest to the zinc smelter, indicating the presence of artificial pollution of these soils with fluorine. The surface layers of soil have more fluoride concentrations as compared to the deeper layers. Evaluation of fluoride levels in local vegetation suggests that leafy vegetables accumulate greater levels than non-leafy vegetables.

Precaution 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.

Clinical significance of this study could be judged by the fact that higher levels of fluoride uptake carry significant health risks. The vegetation and soils in the areas in vicinity of zinc smelter have very high probability of being polluted by fluoride and other wastes released by the facility. Therefore, it is imperative to determine the levels of fluoride in these consumable entities to reduce the risk of human exposure to fluoride hazards.

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