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**Case Report**

# Fluoride Concentration in Ground Water Around an Aluminium Smelter Plant (A Case Study) in Angul–Talcher Industrial Belt, Odisha, India

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**Abstract:** Fluoride is the naturally-occurring stable form of the gaseous element fluorine (F). Fluoride is among the top 15 most abundant components on the Earth's crust [21] and is naturally found in very small amounts in most aquifers in India [23]. An aquifer is an underground unit of saturated earth materials that can provide usable quantities of ground water to a well [5]. This paper gives the result of fluoride measurement in ground water around a major Aluminium smelter plant in India. The concentration of different water quality parameters like pH, electrical conductivity, total alkalinity, bicarbonate, chloride, nitrate, sulfate, total hardness, total dissolved salts, calcium and magnesium are estimated along with fluoride in ground water. Over 216 water samples are taken for analysis for a period of 12 months. The paper also reports the result of correlation coefficient between different water quality parameters.

**Keywords:** Fluoride Concentration, Al-smelter Plant, Ground Water, Physicochemical Parameters, Correlation

## 1. Introduction

Fluorides are normal constituents of water, food and air. Lakes and streams generally contain less than 0.3mg/l of fluoride [16]. Fluorides content in ground water of some areas are higher and depend on the type of the rock through which the water flows [13]. Intake of fluoride in low dose prevents dental caries but fluoride is a cumulative poison under conditions of continuous exposure to sub acute doses [19]. Fluoride is protoplasmic poison [7, 8]. The deleterious effect it has on human and animals are very well known. Fluorosis is a crippling disease caused by the intake of water having higher concentration of fluoride i.e. > 1.5, ppm [6]. The existence of fluoride bearing ground water and fluorosis in India have been reported by many workers. Shortt et. al published the first report on endemic fluorosis in India [18]. The disease was then known to be prevalent in four states in India i.e. Andhra Pradesh, Tamilnadu, Punjab and Uttar Pradesh. Cases of endemic fluorosis have been reported in certain parts of Rajasthan [15, 22, 11, 12, 2, and 3]. No such systematic work has been reported so far regarding the ground water quality of Angul –Talcher industrial belt in the state of Odisha. Besides this literature regarding the fluoride distribution in ground water around an Aluminium smelter plant & related case of fluorosis are scanty [11].

Angul- Talcher Industrial area is in the state of Odisha. This industrial township is reputed due to its vast coal mines, three Thermal power plant (two are owned by NTPC and one Captive Power plant is owned by NALCO), one Aluminum smelter plant (NALCO), some private sector-Ferro-alloy industries & a chemical manufacturing industry. This town is located at about $20^{o}29'$N latitude and $34^{0}16'$E longitude at an elevation of about 73.15 m above mean sea level. Geologically this region is composed of ancient metamorphic rocks like Khondalites, quartzite with charnockite and gneisses forming flanks and valleys. The area under study is mainly covered with Khondalites rock type. Beside coal, the mineral resources comprise of iron, fine clay, chromites, clay, garnet, gold, graphite, kyanite and silimanite, lime stone,

manganese ore etc [9]. This industrial belt is flanked with lot of village surroundings and within the periphery of industries. The area under studies is only limited to localities near to aluminium smelter plant producing 650 tons of aluminium per day by Hall-Heroult's process [10].

The effluent carrying drain from the plant is mixed with a natural stream known as sindajhar which passes through number of villages. Water samples are taken from dug well, tube well and ponds of different villages adjacent to the stream and near to the plant. Fluoride distribution with distance from the aluminium smelter plant is taken into consideration.

## 2. Materials and Methods

After studying the nature of effluent emission from the aluminium smelter plant sampling spots in different villages (1-9) have been chosen adjacent to the stream. Beside this another nine sampling spots (10-18) have been selected near to the plant. All the eighteen sampling spot remained within a radius of 6.15km from this smelter plant (Fig-1). All together 216 water samples have been taken for analysis for a period from March-2014 to February-2015.Samples were taken in pre cleaned polyethylene bottle. Fluoride concentration was measured using Orion ion AnalyserEA-940 with chloride ion selective electrode. pH and electrical conductivity were measured using pH –meter and conductivity bridge(both Systronic make). Chloride, total hardness, total alkalinity, bicarbonate, nitrate, and sulfate were estimated titrometrically as per standard procedure as suggested by APHA [20]. Ca and Mg were determined using AAS (Perkin Elmer (303)). The average value of the analysis result for different parameters has been tabulated in Table-1.

***Table 1.*** *Average Hydro chemical data of Ground water around Aluminium smelter plant.*

| Sampling Station | F | pH | TA | $HCO_3^-$ | $Cl^-$ | $NO_3^-$ | $SO_4^{2-}$ | TH | TDS | EC | Ca | Mg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Kulad Pond – 1 | 2.14 | 7.24 | 208 | 239 | 54 | 42.8 | 31.7 | 310 | 360 | 520 | 30 | 18.7 |
| Kulad Pond – 2 | 1.74 | 7.0 | 164 | 189 | 48 | 30.4 | 26.2 | 210 | 322 | 512 | 36 | 22.4 |
| Kulad Borewell | 1.26 | 7.1 | 172 | 212 | 52.4 | 12.6 | 100 | 248 | 580 | 780 | 46 | 22.8 |
| Kulad openwell | 1.82 | 7.3 | 197 | 234 | 62.2 | 22.8 | 62.4 | 308 | 450 | 604 | 40 | 20.4 |
| Bonda Pond | 2.81 | 7.4 | 168 | 197 | 56.2 | 34.6 | 32.6 | 204 | 410 | 590 | 44.6 | 24.1 |
| Bonda well | 0.77 | 7.4 | 184 | 208 | 48 | 20.2 | 25.4 | 178 | 378 | 498 | 41.0 | 18.0 |
| Bondapond II | 3.31 | 7.38 | 276 | 314 | 188 | 12.8 | 44.6 | 140 | 644 | 920 | 35 | 18.9 |
| Bonda tubewell | 1.21 | 7.7 | 278 | 296 | 67.8 | 11.4 | 126 | 152 | 478 | 610 | 40.6 | 30 |
| Chowadhia Pond | 0.76 | 6.8 | 158 | 182 | 42.6 | 26.6 | 22.4 | 190 | 404 | 480 | 48.2 | 36.6 |
| Banarpalpond – I | 0.71 | 7.2 | 164 | 190 | 54.1 | 16.8 | 28.6 | 194 | 510 | 622 | 54.6 | 32 |
| Banarpalpond – II | 0.70 | 7.3 | 178 | 210 | 56.4 | 18.4 | 32.4 | 198 | 540 | 642 | 58.3 | 36.2 |
| Kuruduluwell | 0.73 | 7.7 | 192 | 246 | 64 | 14.1 | 38.7 | 124 | 442 | 640 | 42.4 | 28.8 |
| Gotamarawell | 0.71 | 7.39 | 70 | 85 | 26 | 12.6 | 12.8 | 150 | 135 | 194 | 30 | 18.7 |
| Langulia Bore well | 0.51 | 6.9 | 110 | 92 | 64.6 | 10.4 | 26.6 | 220 | 398 | 460 | 38 | 24 |
| Tulasipal well | 0.64 | 7.22 | 162 | 197 | 24 | 42.6 | 9.4 | 175 | 238 | 340 | 30 | 18.7 |
| Kandasar well | 0.72 | 7.1 | 160 | 184 | 26.4 | 32.4 | 21.8 | 186 | 324 | 440 | 48.2 | 32.4 |
| Samantapur Pond | 0.86 | 7.2 | 170 | 198 | 24.2 | 16.4 | 89 | 146 | 270 | 320 | 45.4 | 25.2 |
| Balaramprasad well | 0.50 | 7.3 | 172 | 186 | 34.4 | 18.2 | 72 | 148 | 470 | 594 | 42 | 24.6 |

*Except pH and conductivity (in ms) the concentration values of the parameters are in mg/l.

***Table 2.*** *Values of correlation Coefficient among the Different water quality parameters of Ground water around aluminium smelter plant.*

| Param- ters | pH | TA | $HCO_3^-$ | $Cl^-$ | $NO_3^-$ | $SO_4^{2-}$ | TH | TDS | EC | Ca | Mg |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $F^-$ | 0.171 | 0.529 | 0.539 | 0.688 | 0.280 | 0.073 | 0.221 | 0.348 | 0.525 | -0.284 | -0.411 |
| pH | | 0.474 | 0.513 | 0.227 | -0.021 | 0.329 | -0.329 | 0.136 | 0.216 | -0.120 | -0.141 |
| TA | | | 0.972 | 0.635 | 0.161 | 0.521 | -0.033 | 0.627 | 0.690 | 0.019 | 0.021 |
| $HCO_3^-$ | | | | 0.594 | 0.159 | 0.470 | -0.027 | 0.604 | 0.695 | 0.044 | 0.014 |
| $Cl^-$ | | | | | -0.012 | 0.104 | -0.091 | 0.675 | 0.753 | -0.117 | -0.179 |
| $NO_3^-$ | | | | | | -0.104 | 0.555 | -0.101 | -0.036 | -0.368 | -0.273 |
| $SO_4^{2-}$ | | | | | | | -0.040 | 0.404 | 0.357 | -0.153 | 0.052 |
| TH. | | | | | | | | 0.085 | 0.098 | -0.086 | -0.022 |
| TDS | | | | | | | | | 0.959 | 0.461 | 0.267 |
| EC | | | | | | | | | | 0.290 | 0.097 |
| Ca | | | | | | | | | | | 0.834 |

Correlation studies were done among various analyzed parameters using standard statistical package. The correlation matrix is given in table-2.

## 3. Results and Discussion

The fluoride concentration in ground water from tube well, dug well, open pond well area is found to be ranging from a minimum of 0.42 to a maximum of 4.3 mg/l near Bonda sampling station with an average value of 0.50 to a maximum of 3.31mg/l. Out of 216 samples analyzed for fluoride concentration, 52 samples were found to be more than 1.5 mg/l as prescribed by ICMR [14]. The highest fluoride concentration was found in the village Bonda adjacent to the stream (i.e sampling point No-5 and 7). Comparing with first nine sampling station adjacent to the effluent carrying drain, other nine sampling station have a fluoride concentration within desirable limit prescribed by Bureau of Indian Standard [1] and WHO [25] for drinking water.

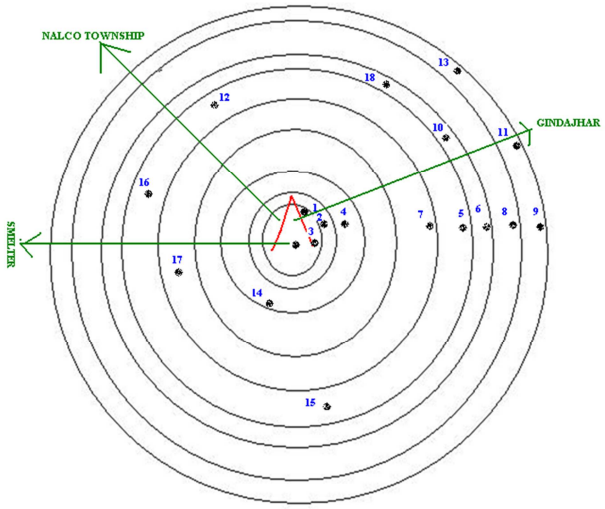


***Figure 1.*** *Sampling site.*

***Table 3.*** *Sampling Points.*

| Sl. No | Sampling point | Sl. No | Sampling point |
|---|---|---|---|
| 1 | Open pond (kulad village) | 10 | Open pond (banarpal village-1) |
| 2 | Open pond (kulad village) | 11 | Open pond (banarpal village-2) |
| 3 | Bore well (kulad village) | 12 | Open well (kurudulu village) |
| 4 | Open well (kulad village) | 13 | Open well (gotamara village) |
| 5 | Open pond(bonda village) | 14 | Open well (langulia beda village) |
| 6 | Open well (bonda village) | 15 | Open well (tulasipal village) |
| 7 | Open pond (Rly.culvert) | 16 | Open well (kandsar village) |
| 8 | Tube well (banda village) | 17 | Open pond (samanthpur village) |
| 9 | Open pond (chowadhia village) | 18 | Open well (balaramprasad) |

To observe the relationship of fluoride with other constituent of water, correlation studies were done and correlation matrix was given in Table-2.

The result revealed that the pH ranged from 6.8 to 7.7. Minimum pH 6.8 was observed in Chowadhiapond and maximum pH 7.7 in Bonda tube well and Kurudulu open well. A positive correlation (r=0.171) was observed between $F^-$ and pH. The relation between fluoride ion and pH is shown in figure 2. According to WHO 1996, the permissible limit of pH is 6.9 to 9.2.A positive correlation as observed between Fluoride and pH (r =0.171).

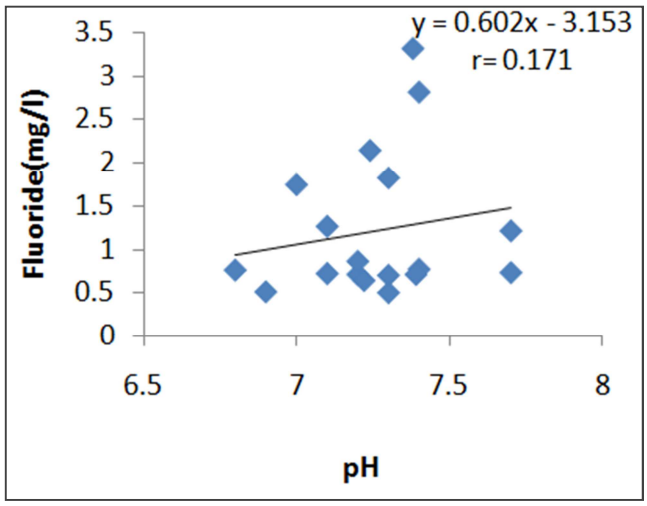


***Figure 2.*** *Relationship between Fluoride and pH.*

Total alkalinity ranged from 70 mg/l to 278 mg/l was observed in the study area. In the present studies, the total alkalinity showed a positive correlation with Fluoride (r = 0.529). This is presented in figure 3.The positive correlation has been reported earlier [24]. The solubility of $CaF_2$ increases with the increase in TA in the ground waters. According to the following reactions:

$$CaF_2 + CO_3^{2-} \longrightarrow CaCO_3 + 2F^-$$

$$CaF_2 + HCO_3^{2-} \longrightarrow CaCO_3 + 2F^- + H_2O + CO_2$$

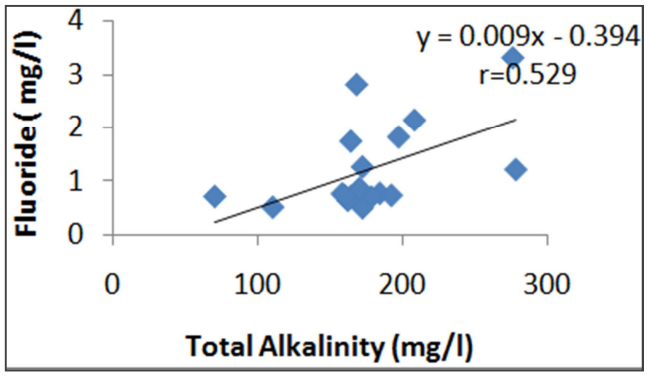


***Figure 3.*** *Relationship between Fluoride and Total alkalinity.*

Total hardness of minimum 124 mg/l and maximum of 310 mg/l were reported in the study area. WHO recommended the safe permissible limit for hardness i.e. 100-500 mg/l. In groundwater, hardness is formed mainly due to carbonate, bicarbonate and chloride of $Ca^{2+}$ and $Mg^{2+}$. All the water

samples collected the TH was within the optimum limit. Calcium hardness ranged from 30 mg/l to 58.3 mg/l and the magnesium hardness ranged from 18.0 mg/l to 32.4 mg/l. Chloride content of ground water samples are 24mg/l ranging upto 188mg/l. Fluoride showed a positive correlation with TH (r = 0.221) which is shown in figure 4.

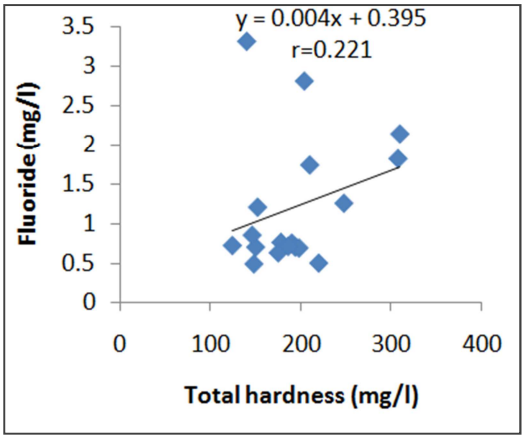


***Figure 4.*** *Relationship between Fluoride and Total hardness.*

A negative correlation was observed between fluoride and calcium (r=-0.284), fluoride and magnesium(r=-0.411). Fluoride was not found related with the depth of water source. It may be due to (i)a negative correlation was observed between fluoride and calcium (ii) fluorine does not occur in free state in nature and it forms fluoride mainly with calcium as fluoropatite [$CaF_2.CaCO_3(PO_4)$], fluespar ($CaF_2$) and apatite($Ca_2F$). The low concentration level of calcium in ground water of this area signifies the above fact that the ground water is not affected by fluoride ore which may be originated from igneous rocks or sedimentary rocks derived from the weathering of igneous rocks [4]. It may be said that the concentration of fluoride in ground water of different villages adjacent to the streams may be due to the effluent of aluminium smelter plant.

An overall correlation analysis is almost a positive correlation between the concentration of fluoride ion with pH, total alkalinity, bicarbonate, chloride, nitrate, sulfate, total hardness, TDS, EC. However $Ca^{2+}$ and $Mg^{2+}$ correlated negatively with fluoride concentration. Out of several parameters only a few were considered for linear regression analysis. The pairs are (a) Fluoride and pH (b) Fluoride and Total Alkalinity (c) Fluoride and Total Hardness. The developed linear relationships fluoride with pH,Total Alkalinity and Total Hardness are given in the equation:

(a) F = (0.0602*pH) – 3.153
(b) F= (0.009*TA) – 0.394
(c) F= (0.004* TH) + 0.395

## 4. Conclusion

The aluminium smelter plant was commissioned in the year 1987. Within the gap of so many years of production time the highest fluoride concentration in the ground water has been reached to a maximum of 4.13mg/l in nearby localities. Moreover many cases of dental and skeletal fluorosis have already been observed among the men and animals, so necessary treatment methods are to be adopted to check high fluoride concentration in the effluent drain of aluminium smelter plant. It may also cause harm to the ecosystem and vegetation, if used for irrigation. So, a ground water management program is suggested for safe and healthy ecosystem.

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