# Correlation studies of fluoride with alkalinity and hardness

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TAMIL NADU IN South India, is identified as a state with high prevalence rate of dental fluorosis. Our studies have confirmed the fluoride endemicity of Dindigdul district of Tamil Nadu. Thirteen out of fourteen revenue blocks of this district have their groundwater sources contaminated with high levels of fluoride (Karthikeyan and Appa rao, 1992). This is further supported by the high prevalence rate of dental fluorosis and the associated symptoms of non-skeletal fluorosis among the people of this region. Three revenue blocks, viz., Shanarpatty, Vadamadurai and Reddiarchatram are chosen as the study area in this investigation. All available drinking water sources of the villages belonging to these three blocks were chemically examined to estimate the quality parameters like pH, Total hardness(TH), Total alkalinity(TA), fluoride, sulphate, chloride and chemical oxygen demand(COD). Correlation analysis was carried out to determine the influence of total alkallinity (TA) and total hardness(TH) on fluoride content of the water and the dependence of these parameters on fluoride toxicity.

## Methodology

All chemical parameters of the water samples were determined using standard methods of water analysis (APHA 1985). pH of the samples was determined using a pH meter 324 of Systronics make and fluoride levels were measured using fluoride ion selective electrode (Model EA 920, ORION USA ).

## Results and Discussion

Influence of total alkalinity (TA) and total hardness (TH) on fluoride content of water samples was studied using linear regression analysis and the results are presented in table 1. Typical stright line plots for the linear relationships between the experimental values of TA and TH with fluoride levels of Vadamadurai are shown in figures 1 and 2.

**Table 1: Correlation coefficient values of TA and TH with fluoride**

| S.No | Block | TA | TH |
|---|---|---|---|
| 1. | Shanarpatty | 0.5751 | -0.0565 |
| 2. | Vadamadurai | 0.3603 | -0.3698 |
| 3. | Rediarchatram | 0.7841 | -0.0584 |

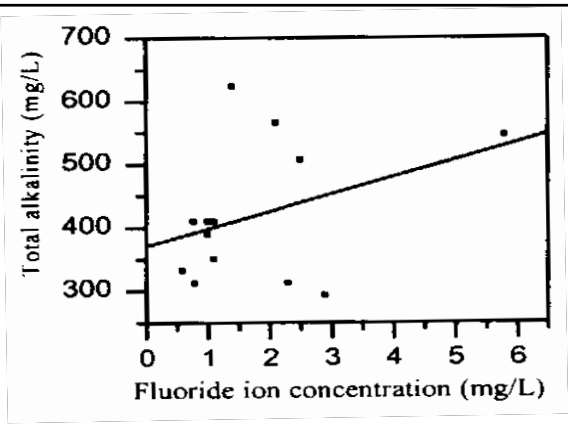


**Fig 1. Vadamadurai block**

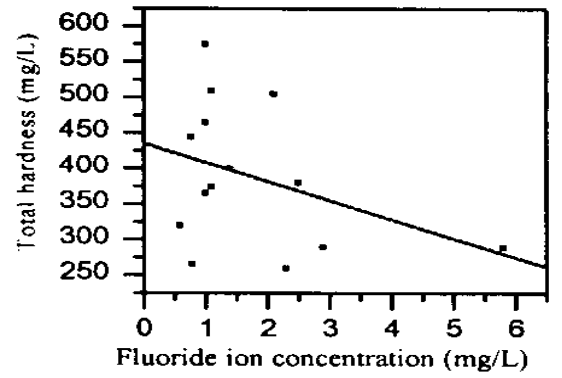


**Fig 2. Vadamadurai block**

Results of the linear regression analysis on the dependence of fluoride on total alkalinity indicate a positive correlation between fluoride content and TA values in all the water samples studied. However a negative correlation exists between fluoride levels and the TH values.

## Influence of Total alkalinity

The positive correlation between the alkalinity and fluoride levels might be due to the release of hydroxyl and bicarbonate ions simultaneously during the leaching and dissolution process of fluoride bearing minerals into the ground waters. That is, more and more leaching of minerals into water increases the fluoride ion concentration with

high levels of alkalinity as well. High fluoride levels are associated with the high concentration of sodium ions because of greater soubility of sodium fluoride in water. Similarly high levels of sodium are associated with increased concentration of bicarbonate ions also and this naturally lead to higher alkalinity levels. The positive correlation of TA and negative correlation of TH with fluoride ions, observed from the experimental data of Vadamadurai are shown in figures 1 and 2.

## Influence of Total Hardness

Water hardness is mainly due to the salts of calcium and magnesium. These metal ions can precipitate fluoride as their respective fluorides. When fluorides are precipitated as calcium fluoride or magnesium fluoride, these compounds may not be absorbed through intestinal absorption and instead they will be excreted by the body through feaces. The level of intake of fluoride through intestinal absorption is not considerable.

The levels of maximum possible calcium and magnesium with fluoride in water can be governed by the solubility product principle (Vogel 1961). The solubility products of calcium fluoride and magnesium fluoride are $3.9 \times 10^{-11}$ and $6.4 \times 10^{-9}$ respectively. The equllibrium for calcium fluoride can be written as,

$$CaF_2 \rightarrow Ca^{2+} + 2\ F^-$$

$$K_{sp} = [Ca^{2+}]\ [F^-]^2 = 3.9 \times 10^{-11}$$

Similarly, the solubility equlibrium of magnesium fluoride is written as

$$MgF_2 \rightarrow Mg^{2+} + 2\ F^-$$

$$K_{sp} = [Mg^{2+}]\ [F^-]^2 = 6.4 \times 10^{-9}$$

This means, only when the product of ionic concentrations of calcium and fluoride in water exceeds $3.9 \times 10^{-11}$ and that of magnesium and fluoride exceeds $6.4 \times 10^{-9}$, these salts will precipate out. Otherwise, when the level of fluoride in drinking water increases, levels of calcium (or magnesium) automatically decreases. However at a given fluoride concentration, the concentration of metal ions can be anything below the maximum permissible levels and to that extent variations in calcium and magnesium are expressed in terms of hardness of water. Higher fluoride levels are therefore associated with lower hardness values.

As fluoride in water is dependent on several contributing factors,the principle of multiple regression analysis was applied to correlate the behaviour of the dependence of fluoride in the three fluoride endemic areas. The multiple regression analysis was done using the following relationships and the results are given in table 2.

$$Y = C + m_1 X_1 + m_2 X_2 + m_3 X_3 \ldots . m_n X_n$$

$$F = C + m_1\ TA + m_2\ TH$$

Where F = fluoride ion concentration

TA = total alkalinity
TH = total hardness
$m_1$, $m_2$ = coefficients and
c = constant

The following conclusions are drawn from the results of multiple regression analysis.

i) The positive sign of the coefficients of TA indicates that it has a direct impact on fluoride ion concentration.
ii) The negative sign of the coefficients of TH indicates that it has an indirect impact on fluoride ion concentration.
iii) Percentage contribution of TA to fluoride in Shanarpatty, Vadamadurai and Reddiarchatram are 84.4, 48.6 and 90.4 respectively while that of TH in the three blocks respectively are 19.6 , 51.4 and 9.6.
iv) The influence of TA on the level of fluoride is appreciably high, when compared to that of TH in all the three blocks.

Reports of several workers (Venkatachalam and Jebanesan, 1998; Gupta, et al, 1994) in the literature lead to conflicting conclusions. Our study reveals that the TH reduces fluoride levels in water as evidenced by negative correlation between these two parameters. However, there are also reports that TH and TA behaved identically exhibiting positive correlation (Venkata-chalam and Jebenasen 1998).

**Table 2: Results of multiple regression analysis**

| Block | v | $R^2$ | SD | $m_1$ | $m_2$ | % contribution | |
|---|---|---|---|---|---|---|---|
| | | | | | | TA | TH |
| Shanarpatty | 26 | 0.6058 | 0.94 | 0.0102 | -0.0019 | 84.4 | 19.6 |
| Vadamadurai | 14 | 0.6425 | 1.15 | 0.0074 | -0.0079 | 48.6 | 51.4 |
| Reddiarchatram | 20 | 0.6458 | 0.50 | 0.0116 | -0.0012 | 90.4 | 9.6 |

v = No. of villages

## Influence of fluoride on the prevalence rate of fluorosis

Table 3 gives the range of fluoride level and the % of incidence of dental fluorosis in the three blocks.

A close examination of tables 2 and 3 reveals that the % contribution of TH on fluoride is high, of the order of 51.4 % at Vadamadurai. This has possibly resulted in the lesser intake of fluoride through drinking water, even though the water fluoride level in this block were more or less the same or even slightly above than those of other two blocks. The comparatively less intake of fluoride through water might have resulted as more of fluoride has been precipitated as calcium and magnesium fluorides due to the high contribution of TH, of the order of 51.4%. The other two panchayats Shanarpatty and Reddiarchatram recorded less contribution of total hardness, of the order of 19.6 % and 9.6 % to the prevalence rate of dental fluorosis with 46.2 and 50.9 respectively.

**Table 3: Prevalence rate of fluorosis and fluoride level**

| S.No | Block | Level of fluoride | | % incidence of dental fluorosis |
|---|---|---|---|---|
| | | max | min | |
| 1. | Shanarpatty | 4.8 | 0.4 | 46.2 |
| 2. | Vadamadurai | 5.8 | 0.17 | 28.9 |
| 3. | Reddiarchatram | 4.3 | 0.5 | 50.9 |

## References

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