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EFFECTS OF FLUORIDE CONTENTS IN GROUND WATER: A REVIEW

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ABSTRACT

Ground water is the major source of freshwater on the earth. Groundwater containing dissolved ions beyond the permissible limit is harmful and not suitable for domestic use. Fluoride beyond desirable amounts (0.6 to 1.5mg/l) in groundwater is a major problem in many parts of the world. The fluorides belong to the halogen group of minerals and are natural constituents of the environment. Fluoride is the most electronegative of all chemical elements and is never encountered in nature in the element form. Though fluoride enters the body through water, food, industrial exposure, drugs, cosmetics, etc., drinking water is the major source (75%) of daily intake. World Health Organization (WHO) and IS: 10500 recommend that the fluoride content in drinking water should be in the range of 1.0 to1.5 ppm.

Intake of more fluoride, results in multidimensional health manifestations, the most common being dental and skeletal fluorosis. This problem is severe in India and need immediate attention of government, donors and philanthropists to save our people. Suitable measures such as defluorinating the groundwater before use and recharging the groundwater by rainwater harvesting need to be practiced to improve the groundwater quality in this area.

Many Defluoridation devices and techniques, which includes Actinated Alumina, Red mud, Nalgonda technique, Magnesia & Montmorillonite have been referred with various limitations.

Comparing all defluoridation devices, the most feasible option for fluoride removal for rural regions seems to be magnesia. It is selective for fluoride removal as it binds well with fluoride ions.

Key words: Fluoride, Groundwater and Defluorination techniques

INTRODUCTION:

Ground water is the major source of freshwater on the earth. Groundwater containing dissolved ions beyond the permissible limit is harmful and not suitable for domestic use. Fluoride beyond desirable amounts (0.6 to 1.5mg/l) in groundwater is a major problem in many parts of the world. [1]

The fluorides belong to the halogen group of minerals and are natural constituents of the environment. Fluorides are mainly found in ground water when derived by the solvent action of water on the rocks and the soil of the earth's crust. Fluoride is the most electronegative of all chemical elements and is never encountered in nature in the element form. It is seventeenth in the order of frequency of occurrence of the elements and represents about 0.06% to 0.09% of the earth's crust. [2] Fluoride is an essential element for life. At low concentrations it is generally believed that fluoride deficiencies can arise but at high fluoride concentrations other deleterious effects can certainly transpire. In relation to drinking water it is generally believed

that too little (<0.5 mg/l) or too much (>1.5mg/l) can affect bone and teeth structure. [3, 4]

Among the water quality parameters, fluoride ion exhibits unique properties as its concentration in optimum dose in drinking water is advantageous to health and if the concentration exceeds the limit, this affects the health. [5] High fluoride concentration in the ground water and surface water in many parts of the world is a cause of great concern. The main source of fluoride in ground water is fluoride-bearing rocks such as fluorspar, fluorite, cryolite, fluorapatite and hydroxylapatite. [6] Also the content in ground water is a function of many factors such as availability and solubility of fluoride minerals, velocity of flowing water, pH, temperature, concentrations of calcium and bicarbonate ions in water. [7, 8]

Though fluoride enters the body through water, food, industrial exposure, drugs, cosmetics, etc., drinking water is the major source (75%) of daily intake. [9] Due to its strong electronegativity, fluoride is attracted to positively charged calcium in teeth and bones. Major health problems caused by fluoride are dental fluorosis, teeth mottling, skeletal fluorosis and deformation of bones in children as well as adults. [10] Excess fluoride affects plants and animals also.

Health Impacts of Fluoride:

Fluoride is well recognized as an element of public health concern. Fluoride is present universally in almost every water (higher concentrations are found in groundwater), earth crust, many minerals, rocks etc. It is also present in most of everyday needs, viz. toothpastes, drugs, cosmetics, chewing gums, mouthwashes and so on.[11, 12] Though a small amount of it is beneficial for human health for preventing dental carries, it is very harmful when present in excess of 1.0 ppm. World Health Organization (WHO) and IS: 10500 recommend that the fluoride content in drinking water should be in the range of 1.0 to1.5 ppm.

Intake of more fluoride, results in multidimensional health manifestations, the most common being dental and skeletal fluorosis. [13, 14] Higher concentration of fluoride also causes respiratory failure, fall of blood pressure and general paralysis. Loss of weight, anorexia, anemia, wasting and cochexia are among the common findings in chronic fluoride poisoning. Continuous ingestion of nonfatal dose of fluorides causes permanent inhibition of growth. Fluoride ions inhibit a variety of enzymes often by forming complexes with magnesium ions and other metal ions. [15-17]

In India, there has been an increase in incidence of dental and skeletal fluorosis with about 62 million people at risk [18] due to high fluoride concentration in drinking water. Dental fluorosis is endemic in 14 states and 150,000 villages in India with the problem most pronounced in the states of Andhra Pradesh, Bihar, Gujarat, Madhya Pradesh, Punjab, Rajasthan, Tamil Nadu and Uttar Pradesh. [19]

Prevalence of Fluorosis:

India is among the 23 nations wherein a large population suffers from dental and skeletal Fluorosis due to high F– concentration in groundwater. [20-22] India has acute public-health problems induced by utilization of groundwater as a source of drinking water. The health problems arising as a result of fluoride (F) contamination are far more widespread in India. Fluorosis was first detected in India, among cattle and humans in Andhra Pradesh. [23] In India, approximately 60–65 million people drink fluoride contaminated groundwater, and the number affected by fluorosis is estimated at 2.5–6 million, predominately children. [24, 25] In India, the excessive presence of fluorides in groundwater is present in nearly 177 districts covering 19 states. It appears that high-well fluoride may exist in many more districts. [26] The prominent states, which are severely affected, are Andhra Pradesh, Rajasthan, Gujarat, Uttar

Pradesh, and Tamilnadu. [27, 28] Earlier reports in different parts of India indicate certain instances of fluorosis. [29] It is cited that dental fluorosis levels of 43% has been reported in Anantapur District of Andhra Pradesh. [30]

Effect of Water Fluoride on human.

Dental and skeletal fluorosis.

Fluoride is among the substances for which there are both lower (0.6 mg/l) and upper (1.2 mg/l) limits of concentration in drinking water, with identified health effect and benefits for human beings. [31] Very low doses of fluoride (<0.6 mg/l) in water promote tooth decay. However, when consumed in higher doses (>1.5 mg/l), it leads to dental fluorosis or mottled enamel and excessively high concentration (>3.0 mg/l) of fluoride may lead to skeletal fluorosis. In general, fluoride content in water between 1.5 and 2.0 mg/l may lead to dental mottling, which is characterized initially by opaque white patches on the teeth and in advanced stages leads to dental fluorosis (teeth display brown to black staining) followed by pitting of teeth surfaces. High manifestations of dental fluorosis are mostly found in children up to the age of 12 years, and skeletal fluorosis [32] may occur when fluoride concentrations in drinking water exceed 4–8 mg/l. The high fluoride concentration manifests as an increase in bone density leading to thickness of long bones and calcification of ligaments. The symptoms include mild rheumatic/arthritic pain in the joints and muscles to severe pain in the cervical spine region along with stiffness and rigidity of the joints. The disease may be present in an individual at subclinical, chronic or acute levels of manifestation. [33] Crippling skeletal fluorosis can occur when the water supply contains more than 10 mg/l of fluoride. [34, 35] The severity of fluorosis depends on the concentration of fluoride in the drinking water, daily intake, continuity and duration of exposure, and climatic conditions.

Neurotoxicity and Neurobehavioral Effects

Animal and human studies of fluoride have been published reporting adverse cognitive and behavioral effects. A few epidemiologic studies of Chinese populations have reported IQ deficits in children exposed to fluoride at 2.5 to 4 mg/L in drinking water.

A few animal studies have reported alterations in the behavior of rodents after treatment with fluoride, but the committee did not find the changes to be substantial in magnitude. More compelling were studies on molecular, cellular, and anatomical changes in the nervous system found after fluoride exposure, suggesting that functional changes could occur. These changes might be subtle or seen only under certain physiological or environmental conditions. More research is needed to clarify the effect of fluoride on brain chemistry and function.

Endocrine Effects

The chief endocrine effects of fluoride exposures in experimental animals and in humans include decreased thyroid function, increased calcitonin activity, increased parathyroid hormone activity, secondary hyperparathyroidism, impaired glucose tolerance, and possible effects on timing of sexual maturity. Some of these effects are associated with fluoride intake that is achievable at fluoride concentrations in drinking water of 4 mg/L or less, especially for young children or for individuals with high water intake. Many of the effects could be considered subclinical effects, meaning that they are not adverse health effects. However, recent work on borderline hormonal imbalances and endocrine-disrupting chemicals indicated that adverse health effects, or increased risks for developing adverse effects, might be associated with seemingly mild imbalances or perturbations in hormone concentrations. Further research is needed to explore these possibilities.

Effects on Other Organ Systems

The committee also considered effects on the gastrointestinal system, kidneys, liver, and

immune system. There were no human studies on drinking water containing fluoride at 4 mg/L in which gastrointestinal, renal, hepatic, or immune effects were carefully documented. Case reports and in vitro and animal studies indicated that exposure to fluoride at concentrations greater than 4 mg/L can be irritating to the gastrointestinal system, affect renal tissues and function, and alter hepatic and immunologic parameters. Such effects are unlikely to be a risk for the average individual exposed to fluoride at 4 mg/L in drinking water. However, a potentially susceptible subpopulation comprises individuals with renal impairments who retain more fluoride than healthy people do.

Genotoxicity and Carcinogenicity

Many assays have been performed to assess the genotoxicity of fluoride. Since the 1993 NRC review, the most significant additions to the database are in vivo assays in human populations and, to a lesser extent, in vitro assays with human cell lines and in vivo experiments with rodents. The results of the in vivo human studies are mixed. The results of in vitro tests are also conflicting and do not contribute significantly to the interpretation of the existing database. Evidence on the cytogenetic effects of fluoride at environmental concentrations is contradictory.

Whether fluoride might be associated with bone cancer has been a subject of debate. Bone is the most plausible site for cancer associated with fluoride because of its deposition into bone and its mitogenic effects on bone cells in culture. In a 1990 cancer bioassay, the overall incidence of osteosarcoma in male rats exposed to different amounts of fluoride in drinking water showed a positive dose-response trend. In a 1992 study, no increase in osteosarcoma was reported in male rats, but most of the committee judged the study to have insufficient power to counter the evidence for the trend found in the 1990 bioassay.

Several epidemiologic investigations of the relation between fluoride and cancer have been performed since the 1993 evaluation, including both individual-based and ecologic studies. Several studies had significant methodological limitations that made it difficult to draw conclusions. Overall, the results are mixed, with some studies reporting a positive association and others no association.

On the basis of the committee's collective consideration of data from humans, genotoxicity assays, and studies of mechanisms of action in cell systems (e.g., bone cells in vitro), the evidence on the potential of fluoride to initiate or promote cancers, particularly of the bone, is tentative and mixed. Assessing whether fluoride constitutes a risk factor for osteosarcoma is complicated by the rarity of the disease and the difficulty of characterizing biologic dose because of the ubiquity of population exposure to fluoride and the difficulty of acquiring bone samples in nonaffected individuals.

A relatively large hospital-based case-control study of osteosarcoma and fluoride exposure is under way at the Harvard School of Dental Medicine and is expected to be published in 2006. That study will be an important addition to the fluoride database, because it will have exposure information on residence histories, water consumption, and assays of bone and toenails. The results of that study should help to identify what future research will be most useful in elucidating fluoride's carcinogenic potential.

Sorption

A sorption process is normally designed in a plug flow filter column, including a medium that has a certain capacity of absorption, adsorption or ion exchange of the fluoride. This process requires recharge or regeneration of the medium upon saturation. Numerous media are known to have defluoridation properties.

However, due to capacity, availability and subsequent water quality limitations only bone char and activated alumina are worth mentioning. The plants are based on bone char sorption,

which is the process of choice if acceptable by the community. Alternatively, similar set-ups can be utilized in the activated alumina process. This is often preferred e.g. in strictly vegetarian societies that consider the use of (cow) bone char as unethical.

Nalgonda [36] has developed its own method of defluoridation which is cheap effective alternative depending upon the benefits to cost ratio. It's easy for installation in rural area to avoid flourosis disease to certain extent however it needs to be revised.

A co-precipitation process is often carried out in batch containers, where the precipitating chemicals are totally mixed with the raw water. This process requires filling of water and chemicals, mixing and settling and subsequent withdrawal of the treated water and the produced sludge. In the so-called *Nalgonda technique* high dosage of alum and lime are used in a coagulation/sedimentation process, where the precipitation of aluminium hydroxide instantly binds a part of the water fluoride.

Nalgonda process design limitations.

The Nalgonda process design is complicated and must be confirmed empirically. This is mainly because of the co-precipitation that lacks stoichiometry, the great variation in media quality and solubility and the efficiency being dependent on the raw water quality, in particular the fluoride concentration, pH and the alkalinity. Adding alum as done in Nalgonda technique may not be ideal because aluminum is being incriminated in the causation of Alzheimer's disease in the west.

Discussion and Conclusion:

Groundwater containing dissolved ions beyond the permissible limit is harmful and not suitable for domestic use. Fluoride concentration in groundwater varies with the groundwater level fluctuation. Two distinct types of relationship between the groundwater level and fluoride concentration were observed. In wells where the water table occurs at shallow depths, which are from 0 to 4.5 m below ground level, the fluoride concentration was high when the water level was low and the fluoride concentration decreases with the rise in water table. Relative high fluoride concentration during the lowering of water table is because of possible direct evaporation of groundwater from the wells. The fluoride concentration was low when the water level rises due to dilution by fresh rainwater recharge.

Weathering of rocks and leaching of fluoride bearing minerals are the major reasons which contribute to elevated concentration of fluoride in groundwater. The other important natural phenomenon that contributes to high fluoride is evaporation. Thus, the granitic rocks of Nalgonda possess the highest fluoride content than in any other parts of the world. Hence, the major reason for elevated groundwater fluoride concentration in this area must be due to weathering of rocks and rock–water interaction.

Fluorosis is dreaded disease caused by consumption of excess fluoride. This is caused chiefly through consumption of water having excess fluoride content. The WHO standards prescribe 1.5 PPM as maximum level of fluoride in drinking water. However deep bore wells do carry excess fluoride causing various bone and physical deformities.

This problem is severe in India and need immediate attention of government, donors and philanthropists to save our people. Suitable measures such as defluorinating the groundwater before use and recharging the groundwater by rainwater harvesting need to be practiced to improve the groundwater quality in this area.

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REFERENCES

1. K. Brindha. R. Rajesh. R. Murugan. L. Elango (2010). Fluoride contamination in groundwater in parts of Nalgonda District, Andhra Pradesh, India. *Environ Monit Assess*, DOI 10.1007/s 10661–010–1348-0.
2. Wedepohl, K.H.: Hand book of geochemistry. Springerverlage berlin. (Ed.: Heidelberf). New York. 2, 9 K-1 pp. (1974).
3. Edmunds, W.M. and P.L. Smedley: Fluoride in natural waters occurrence, controls and health aspects. *In*: Medical geology. New York (Ed.: O.Selenus). Academic Press (2003).
4. Edmunds, W.M. and P.L.Smedley: Ground water geochemistry and health: An overview. *In*: Environmental geochemistry and health (Eds: J.D. Appleton, R. Fuge, G.J.H. Mc call). Special Publication 113. London: Geological Soceity. Pp. 91-105 (1996).
5. Venkata Moham, S., Nikhila, P. and Reddy, S.J., Determination of fluoride content in drinking water and development of a model in relation to some water quality parameters, *Fresenius Envir Bull*, 4, 297-302 (1995).
6. Meenakshi, V.K., Garg.Karik., Renuka and Anju Malik, Ground water quality in some villages in Haryana, India: Focus on fluoride and fluorosis, *Jounal Hazardous Material*, 106B, 85-97(2004).
7. Agarwal, V., Vaish, A.K. and Vaish, P, Ground water quality: Focus on fluoride and fluorosis in Rajasthan, *Curr. Sci*, 739, 743-746 (1977).
8. Chandra, S.J., Thergaonkar, V.P. and Sharma, R., Water quality and dental fluorosis, *Ind. J. Pub*, H115(25), 47-51(1981)
9. Sarala, K. and Rao P.R., Endemic fluorosis in the village Ralla Anantapuram in Andhra Pradesh – An epidemiological study, Fluoride, 26, 177-180 (1993).
10. Susheela, A.K., Kumar, A., Betnagar, M. and Bahadur, M., Prevalence of endemic fluorosis with gastro-intestinal manifestations in people living in some north-Indian villages, *Fluoride*, 26, 97-104 (1993).
11. Thatte, C.D. Matching of water supply with growing demands. J. IWWA. 1994; 26(2): pp 67-71.
12. Subba Rao, N., Prakasa Rao, J. Niranjan Babu, P. Chandra Rao P. and Krishna Rao, G. Hydrogeochemical zoning in crystalline terrain and its significance to water quality. Jour.Geol. Soc. India, Vol. 49, No. 6, 1997: pp 715-719.
13. Hubner, M.; Geochemische interpretation non fluorid/hydroxide Austauscheversuchen and Tonmineralen. Ber Dentsch. Geo. Geol. Wise. B.Miner. LagerstattenForsch,1969:pp 1415.
14. Ramamohana Rao, N. V. and Rajyalakshmi, K. Studies of water quality and incidence of fluorosis in Andhra Pradesh. Proceedings of the Symposium on Fluorosis, Hyderabad. 1974: pp 477-486.
15. Andezhath, S. K., Susheela, A. K., & Ghosh, G. (1999). Fluorosis management in India: The impact due to networking between health and rural drinking water supply agencies, *AHS-AISH* Publication, 260, 159-165.
16. Pillai, K. S., & Stanley, V. A. (2002). Implications of fluoride-an endless uncertainty. *Journal of Environmental Biology*, 23, 81-87.
17. Ramesam, V. and Rajagopalan, K. Fluoride ingestion into the natural water of hard rock areas, Peninsular India. Jour. Geol. Soc. India. Vol. 26, 1985: pp 125-132.
18. Rao, R. J. and Naidu, M. G. C. Geochemistry of high fluoride natural waters if Jaggaiahpalem, fluorosisendemic village near Visakhapatnam district, Andhra

Pradesh, Inst. Symposium on Recent researches and applications of Geochemistry, Patna, India.1973: pp 6.

19. Subba Rao, N. Factors affecting optimum development of groundwaters in crystalline terrain of the Eastern Ghats, Visakhapatnam area, Andhra Pradesh, India, Jour. Geol. Soc.India. Vol. 40, No. 5, 1992: pp 462467.
20. UNICEF, State of the art report on the extent of fluoride in drinkingwater and the resulting endemicity in India. Fluorosis Research and Rural Development Foundation for UNICEF, NewDelhi, 1999.
21. WHO, Fluoride in drinking water, World Health Organization, Geneva, 2006.
22. Pillai, K. S. and Stanley, V. A., Implication of fluoride – an endless uncertainty. *J. Environ. Biol.*, 2002, 23, 81–87
23. Short, H. E.,Mc Robert. R., Bernard, T. W.,&Mannadinayar, A. S. (1937). Endemic fluorosis in the Madras, Presidency. Indian Journal of Medical Research, 25,553–561.
24. Athavale, R. N., & Das, R. K. (1999). Beware! Fluorosis is zeroing in on you. *Down to Earth, 8*, 24–25.
25. Subba Rao, N. (2008). Fluoride in groundwater, Varaha river basin, Vsakhapatnam district, Aandhra Pradesh, India. *Environmental Monitoring Assessment, 152*,47–60.
26. Susheela, A. K. (2001). *A treatise on f luorosis* (p. 15). Delhi: Fluorosis Research and Rural Development Foundation.
27. Muralidharan, D., Nair, A. P., & Sathyanarayana, U.(2002). Fluoride in shallow aquifers in Rajgarh tehsil of Churu district Rajasthan—An arid environment.*Current Science, 83*, 699–702
28. Subba Rao, N. (2008). Fluoride in groundwater, Varaha river basin, Vsakhapatnam district, Aandhra Pradesh, India. *Environmental Monitoring Assessment, 152*,47–60.
29. Reddy, N. B., & Prasad, K. S. S. (2003). Pyroclastic fluoride in groundwaters in some parts of Tadipatri Taluk, Anantapur District, Andhra Pradesh. *Indian Journal of Environmental Health, 45*, 285–288.
30. ISI, Drinking water standards, Table 1. Substance and characteristics affecting the acceptability of water for domestic use 18,10500. Indian Standard Institution, New Delhi, 1983.
31. Apambire, W. B., Boyle, D. R. and Michel, F. A., Geochemistry, genesis and health implications of floriferous ground waters in the upper regions of Ghana. *Environ. Geol.*, 1997, 33, 13–24.
32. Teotia, S. P. S. and Teotia, M., Endemic skeletal fluorosis: clinical and radiological variants. *Fluoride*, 1988, 21, 39–44.
33. World Health Organization, Fluorides and human health. World Health Organization Publ., Monogr. Ser. 59, 1970, WHO, Geneva.
34. Boyle, D. R. and Chagnon, M., An incidence of skeletal fluorosis associated with groundwaters of the Maritime Carboniferous Basin, Gaspe Region, Quebec. *Can. Environ. Geochem. Health*, 1995, 17, 5–12.
35. Reddy, N. B., & Prasad, K. S. S. (2003). Overview on defluoridation Andhra Pradesh. *Indian Journal of Environmental Health, 45*, 285–288.
36. www.nalgonda.com