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Review

TREACHEROUS IMPACTS OF HYDROGEN FLUORIDE AROUND BRICK KILNS: A REVIEW

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ABSTRACT

A hydrogen fluoride emission from the brick kiln is the global rising issue. It acts as causative agent for various problems related to the soil, water, vegetation and ultimately the human health. Fuel burning in the kilns release very hazardous gases that damages the natural surrounding environment. Fluoride pollution coupled with high rainfall, lower the cation exchange capacity of soil and also effects the photosynthetic activity of plants. Fluoride is also used as natural contaminant in drinking water in many developing countries. Some developed countries revised their quality controls to ensure the fluoride free environment after annual toxicity reports. Hydrogen fluoride leads to the neural disorders in the children; very few are reported in the adults. This review paper focuses on the effects of the hydrogen fluoride on the soil, water, vegetation and the human health.

INTRODUCTION

Bricks are the primary building material used in most of the world. Brick kiln is the poorly characterized industrial sector of the developing countries. Bricks are fired in several different types of the brick kilns according to resources and available infrastructure. But the artisanal brick kiln is the most common type used in Pakistan and other developing or low-income countries. They use coal, plastic trash, motor oil and tires to fire bricks, leading to the poor air quality. These kilns pump out the greenhouse gases, hydrogen fluoride, sulphur dioxide and many other such pollutants in the air, causing menacing effects through soil, water, air and many other sources to the kiln workers, surrounding communities and even a threat to farther areas (Bieckel J., 2014).The available literature is summarized to perform a review article, included the maximum published studies on the increased fluoride exposure especially around the brick kilns. This article majorly focus the developing and the low-income countries and have been included their risk assessment reports.

EFFECTS OF FLUORIDATED WATER

The ground water quality is degrading due to poor industrialization, urbanization and poor agricultural practices adopted around the globe. In drinking water, fluoride is generally present as natural contaminant, contamination of water depends on the concentration of the fluoride present in water and it changes by variations in the geographical conditions (Ap Rees T et al., 1987). High fluoride concentrations in drinking water were found hilarious, recently reported by National Research Council (NRC 2006) which may be of concern. Due to its threatening effects, World Bank, World Health Organization, UN and many other organizations have turned their focus towards this rising but neglected issue. Many studies have been conducted on various aspects of the hydrogen fluoride. Four recent studies were conducted (Li XS, Zhi JL, Gao RO 1995; Zhao LB et al., 1992) which were reported by National Research Council of 2006. Out of which two (Li XS, Zhi JL, Gao RO 1995; Lu Y et al., 2000) were added in their most recent fluoride annual edition. As a rejoinder to the recommendations of the NRC (2006), the U.S. Department of Health and Human Services (DHHS) has put forward the new fluoride range in drinking water 0.7–1.2 mg/l to the recommended level of to 0.7 mg/L. While fluoride limit is set at 4.0 mg/l by the U.S. Environment Protection Agency in

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reviewing the quality controls of the drinking water recently (U.S. EPA. EPA and HHS 2015). In most of the developed and industrialized countries, fluoride concentrations are not higher than 1mg/L in usual community drinking water, where it is difficult to find such population groups ranging in different levels of fluoride. As a public health remedy, the water supplies contain small amount of fluoride, to reduce tooth decay (World Bank 2006).

(http://siteresources.worldbank.org/INTEAPREGTOPENVIRONMENT/Resources/China_WPM_final_lo_res.pdf)

A study was conducted for the contaminated groundwater and the soil in Punjab, Pakistan. Main focus area included Lahore and some adjacent areas. Farooqi has been reported that at the depth of 20 to 27 meter, heavily polluted (F- concentrations of 22.8 mg/L) groundwater was found in a shallow aquifer. While high concentrations of fluoride were found in deep aquifers. Kalalanwala village was highlighted as the most contaminated site in the whole study area (Farooqi A et al., 2007).

HEALTH EFFECTS

Fluoride is neurotoxicity. Neurotoxicity caused when fluoride was tested on the laboratory animals, memory loss and effects on learning were reported (Mullenix PJ et al., 1995; Chioca LR et al., 2008). Because development of brain is very fast up to 5 years and the fluoride attacks very quickly on the developing stage of brain. That's why the children's brain are more susceptible to the toxicity caused by fluoride exposure, may possibly leads to the permanent damage to the human brain (Grandjean P and Landrigan P, 2006). It can also attack the fetus in the mother womb, due to its ability to readily cross the placental membrane (Cotton FA et al., 1987). In adults, acute poisoning was reported (NRC (National Research Council)).

Several epidemiological studies were conducted using different sensitivity tests (Binet IQ test, Raven's test, the CRT-RC or Wechsler Intelligence test) or screening tests for the contaminated drinking water while some also include the fluoride exposures from the coal burning. Reference areas or groups were selected for the comparative studies. Table 1 include the studies conducted for the contaminated drinking water and the exposure to the fluoride impact.

Above table about the different studies conducted in developing countries on students IQ level has proved that fluoride effect the children IQ level. Through these studies children of different age group were treated with fluoride via drinking water which shown their lower IQ level as compare to those children (reference group) who were given fluoride-free drinking water. Except one study conducted by Li et. (2010) which showed that there is no difference of IQ level between referenced group of children

Table 1. Fluoride exposure to different samples and children's outcomes.

Reference	Location	Age	Sample	Fluoride range	Assessment	Result
Zhang et al. 1998	Xinjiang, China	Below 10 years	Fresh Water	Not specified	Japan IQ Test	Fluoride effected children have lower IQ score as compare to reference group
Lu et al. 2000	Tianjin, China	10–12	Drinking water	3.15 mg/L	CRT-RC	Fluoride effected children have lower IQ score as compare to reference group
Hong et al. 2001	Shandong, China	8–14	Drinking water	2.90 mg/L (high); 0.75 mg/L (lower)	CRT-RC	Fluoride effected children have lower IQ score as compare to reference group
Seraj et al. 2006	Tehran, Iran	Not specified	Drinking water	2.5 mg/L (high); 0.4 mg/L (lower)	Raven's test	Fluoride effected children have lower IQ score as compare to reference group
Wang et al. 2006	Shanxi, China	8–12	Drinking water	5.54 ± 3.88 mg/L (high); 0.73 ± 0.28 mg/L (lower)	CRT-RC	Fluoride effected children have lower IQ score as compare to reference group
Fan et al 2007	Shaanxi, China	7–14	Drinking water	1.14–6.09 mg/L (high); 1.33–2.35 mg/L (lower)	CRT-RC	Fluoride effected children have lower IQ score as compare to reference group
Li et al. 2010	Henan, China	7–10	Fresh water	2.47 ± 0.75 mg/L	CRT-RC	No difference of IQ level between children of reference and fluoride effected groups
Poureslami et al. 2011	Iran	6–9	Fresh water	2.38 mg/L	Raven's test	Fluoride effected children have lower score as compare to reference group

and fluoridated water drinking group of children. Researcher revealed through this study that IQ level (5.19%) among children affected by fluorosis is not significantly different than IQ level (5.7%) found among normal children.

Maximum Permissible Limit (MPL) of fluoride concentration in drinking water is 1.5 mg/L set by World Health Organization. However developing countries following their own national standards for fluoride permissible concentration in drinking water. Like India has MPL 1.2 mg/L for fluoride in fresh drinking water. Whereas Pakistan is following the same MPL for fluoride in Drinking water i.e. 1.5 mg/L. Besides China has national standard for fluoride in drinking water is 1mg/L. Because china has large area with excess fluoride in water which caused fluorosis among inhabitants.

PHYTOTOXIC EFFECTS OF FLUORIDE

Rocks and soils contain Fluoride as their common constituent. In rocks, high F^-concentration was present in the soil due the disintegration of fluoride rich minerals (Tripathy S et al., 2005). Implications of several diseases have been arising by the combustion of coal, contaminating the soil and water by F^- in most populated areas of China (Finkelman RB et al., 2002; Zheng B et al., 1996). Contaminated soil with F^- indicated as a groundwater contaminant by seeping through the soil entering in the groundwater. Coal and fertilizers applied to the soil also contained the As^- and F^- in them. Terrace soils bear a high concentration of F^- having pH up to 8 and mean concentration of 4mg/kg while low concentration in the alluvial sediments (http://yosemite.epa.gov/opa/admpress.nsf/bd4379a92ceceeac8525735900400c27/86964af577c37ab285257811005a8417!OpenDocument.,//siteresources.worldbank.org/INTEAPREGTOPENVIRONMENT/Resources/China_WPM_final_lo_res.pdf). Oxidizing conditions allow to dissolve the F^- adsorbed on the soil produces highly alkaline water which leads to the intensive mineral weathering. Combusted coal, manufacture of bricks, industrial waste and fertilizers indicated as the most anthropogenic sources for accumulation of F^- in the soil.

Over the past 30 years fertilizer consumption has increased three times, 1 million tons in 1981, twice in 1993, and thrice in 2003. Consumption of fertilizer nutrients will increase at the rate of 2–3% per year in the next 10 by years according to the projection data (Food and Agriculture Organization of the United Nations).

Low cation exchange capacity of soil coupled with high rainfall in some area, helps in exhausting the mitigation capacity of soils leading to soil acidification. In 20th century, it was reported that in some soil samples of Sweden the soil acidification was less than one pH unit and below pH 4 was also found in some cases (Tamm CO and Hallbacken L., 1988). Fluoride readily enters or crosses the cell membrane of the plants because at low pH, fluoride is found in its ionic form. Over the past 30 years, extensive acidification of Swedish forest soils was also reported (Horner JM and Bell JNB., 1995). some highly developed countries like United Kingdom, are also facing widespread soil acidification problems. Fluoride emissions from different sources in the industrial area has significant role in the acidification process. It mainly depends on the deposition method of the pollutant in the soil, either dry deposition or wet deposition. According to the studies, dry deposition is more crud to soil acidification than wet deposition (Nilsson J., 1988). The areas around the industrial premises are more rapidly suffering from the soil acidification (Wainwright M et al,. 1982). These cases are more frequently reported on the unplanned industrial sites and the urban sites having poor quality soil and less soil deposition levels. Industrial fluoride pollution was reported, leads to very high fluoride toxic levels in various plant species (Quick P et al., 1989). The first documented evidence was provided by Horner (1995) that acid rain and fluoride may act simultaneously in inhibiting plant growth via soil deposition. Some field experiments, pot trials and bioassay techniques were applied to conduct this study (Horner JM and Bell JNB., 1995).

Acid rain is globally an agitating issue about the vegetation damage from the last three decades. Several researches have been carried out, and decisive conclusion is that when some pollutants or damaging factors combined with the acid rain, they result in vegetation loss. Acid rain alone is not a major threat to vegetation (Wainwright et al., 1982). Near the industrial emission sources, elevated concentrations of fluorides in plants and soils were found, by which high vegetation damage was repoted (Quick P et al., 1989). Direct emissions of fluoride from industries is much more damaging than the deposited fluoride in soils. Natural soils have several minerals such as Calcium as major one while some others as iron (III) hydroxide, which can breakdown or fix these fluorides. But due to poor soil quality at some areas, they are unavailable (Yang S F and Miller G W., 1963). Visible damage was caused to *Oryza Sativa* (rice) plants near brick kiln and ceramic works, fluoride concentrations were found up to 3950 ppm in highly damaged plants (Sun EJ and Su HJ., 1985).

In one study, concentrations of organic acids and amino acids were found greater in leaves of fluoride-fumigated soya-bean plants than leaves from control plants. These acids could have accumulated due to some combined or alternative factors, for example more acids could be released due to increased rate of glycolysis, and less utilization of these acids due to blockages may lead to protein degradation. As fluoride plays an important role in stimulating the carboxylation process. A correlation analysis between fluoride fumigated leaves and the normal to compare their rate of CO2 fixation or glycolysis and the increased rate of acids (Yang S F and Miller G W., 1963).

Fluoride mainly targets the photosynthetic activity of the plants by targeting the photosynthetic enzymes such as chloroplast ATPase, RUBP carboxylase and sucrose synthetics. NaF and HF treatments were used for this study (Boese SR et al., 1995). For the chlorophyll concentrations, Chl *a* fluorescence was used by applying the absorptions coefficients of Wellburn and Lichtenthaler (1984) (Wellburn A R and Lichtenthaler H., 1984). Higher plants contain a considerable amount of PPi which could operate as energy donor in their cytosolic metabolism (Black CC et al., 1985; //www.atsdr.cdc.gov/toxprofiles/tp11.pdf). In some studies, CO2 (C^{14}) was applied to leaf discs to measure the starch and sucrose levels in higher plants (Sun EJ and Su HJ., 1985). The effect of fluoride was studied on the spinach leaves by investigating its enolase activity. Because carbohydrate metabolism is inhibited on the enolase site by fluoride so that enolase was considered as reference (Warburg E and Christian., 1942).Waso

Toxicity of fluoride in oats *Avena sativa* (oats) and *Lycopersicon esculentum* (tomatoes was studied in relation with its plant uptake capacity. Different solutions with varying concentrations of fluoride were used. Tomatoes were found more sensitive to fluoride than oats. Small ionic radius and high electronegativity of F^- influence the plant uptake, by effecting its root and shoot growth (Stevens DP et al., 1998). In this study, complex of Fluoride with calcium (CaF_2) proposed as an alternative mechanism to fluoride membrane (Cotton FA et al., 1987). High concentration of fluoride was found in fruit juices and vegetables. A study was conducted in the region of Kenya. 26 samples of fruit juices were analysed, out of which 18 samples contain more than 1 mg/l (permissible limit by WHO) of fluoride (Njenga LW and Kariuki DN., 2004). Water supply for these fruits and vegetable plants was concluded as the causative agent for this problem because that water source was contaminated with high concentration of fluoride from 2.5 mg/l to 5.5 mg/l (Gitonga JN et al., 1984; World Health Organization (WHO).).

CONCLUSION

Literature suggested that fluoride has adverse impact on plants, animals and humans health. Fluoride damages the plant marginal and axes leave tissues and damaging chlorophyll production resulting in to plant growth reduction. While fluoride effect the developing brain of the children, and leads to the neurotoxicity and also cause dental fluorosis. WHO has set a permissible limit for the fluoride i.e. 1.5mg/L, but at lower concentration even from permissible limit like at 0.23mg/L fluorosis has been reported in developing countries. In this regard quality control for water must prohibit the use of fluoride as a contaminant in drinking water and propose some alternatives for the remedy of the tooth decay.

Present study provide reference approach for the further future studies on the fluoride. Future researches should be provided the genetics and dose-response relationship of the children's exposure over time, with their parental samples to propose the preventive measures for the people living in the high fluoride contaminated environment.

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