4

Impact of Geoenvironmental Hazards on Ground Water and Human Health: the Mechanism and Management

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1. Introduction

Management and protection of the ground water is most important, since ground water is considered as the most precious resource in the earth. Once this vital resource is contaminated it will cause several ecological disturbances. In recent years the large-scale occurrence of ground water contamination by some inorganic pollutants like arsenic and fluoride and the associated human sufferings is a threat of this millennium. The severity, magnitude and spread of such problem over the world have reached at an alarming stage (1,2). The source of contamination of ground water is primarily geogenic in origin, with some anthropogenic activities accelerating the problem. The actual mechanism of leaching of the contaminants from the parent minerals to the aquifers is not understood. Still it is clear that indiscriminate use of ground water definitely aggravate the problem. It is estimated that at least sixty four million people in the world are suffering from fluoride related health problem (3) and more than four million people in India, in the state of West Bengal alone (4) are developed the symptom of arsenic toxicity. The toxins like arsenic and fluoride find their route and accumulate through food chain (5). The observation that the menace is spreading over the newer areas and some other toxins similarly could appear in the ground water is a real concern to society. This points to the need for a continuous and critical evaluation of ground water quality before its use as drinking and irrigation purposes.

2. Source

Both arsenic and fluoride are widely distributed throughout the earth's crust and are introduced into ground water through the dissolution of minerals and ores as well as a result of erosion from local rocks. Industrial effluents also contribute arsenic and fluoride to water in some areas. Arsenic and fluoride are also used commercially, e.g., in alloying agents and wood preservatives. Combustion of fossil fuels is a source of the contaminations in the environment through disperses atmospheric deposition. Arsenic and fluoride from water, sediment, soil and rocks can concentrate in living organisms.

Among the different sources of contaminations the pollution of ground water through geological sources are very crucial. The complex pathway and mobilization pattern make the situation very critical.

3. Natural occurrence

Arsenic and fluoride are widely distributed in a variety of minerals. The most abundant arsenic mineral is Arsenopyrite (FeAsS), although Realgar (AsS) and Orpiment (As_2S_3) are not uncommon (6). The main sources of fluoride are Fluorite (CaF_2), Fluorapatite [$3Ca_3(PO_4)_2.CaF_2$], Cryolite (Na_3AlF_6), Magnesium Fluoride (MgF_2) and replacement of ions of crystal lattice of micas and many other minerals. Fluoride and arsenic contents in the material crusts vary considerably. Generally sedimentary materials contain greater arsenic concentrations than igneous materials, which are richer in fluoride contents compared to the former. Fluoride occurs (7) in calcium granite (500 mg/L), in alkaline rocks (1200 mg/L), in shells (750 mg/L) and in sandstone (270 mg/L). On the other hand, arsenic occurs mainly in basalt (<1÷113 mg/kg), shale and clays (<1÷500 mg/kg), sandstones (<1÷120 mg/kg) and phosphorites (3÷100 mg/kg). It is noteworthy that while arsenic occurs in alluvial sediments, fluoride is found in non-alluvial sediments.

4. Status and background

During 1980's a new type of incurable skin disease among the rural population was first noticed which was detected as arsenicosis during July 1983. The recent report shows that about 26 countries are affected with arsenic pollution in ground water of which four South-Asian countries are worst affected. In order of magnitude, these are Bangladesh, India (West Bengal), China and Taiwan (8,9). At present 29 countries in the world are reported to be affected with fluoride contamination in ground water arising only from geoenvironmental reasons (10). The arsenic related ground water problem in West Bengal, India have received considerable attention in the last decade, while a relatively poor attention has paid to fluoride problem. The health impacts are serious in both the cases; the health damage for each case is irreversible and practically no effective medical treatment is available for the cure.

In India a large number of population is suffering from arsenic and fluoride toxicity. A recent study conducted by the UNICEF on the extent and magnitude of the fluorosis problem indicated that at least 213 districts of 18 states, including four districts of West Bengal, are affected. The scale of arsenic problem is serious in West Bengal, India, where nine districts out of eighteen are badly affected. The average of high arsenic concentration is found 4.5 times of the limit of tolerance by human body (0.05 mg/L, as per Indian Standards) and at places goes up 7 times of the latter. The highest fluoride concentration in ground water has been found to be 19 mg/L (maximum permissible limit 0.5 mg/L, as per WHO) in West Bengal. The ground water fluoride concentration in Haryana is found to be more than 84 mg/L, which is highest in India. The growth pattern of arsenic affected zones of West Bengal is presented in Figure 1.

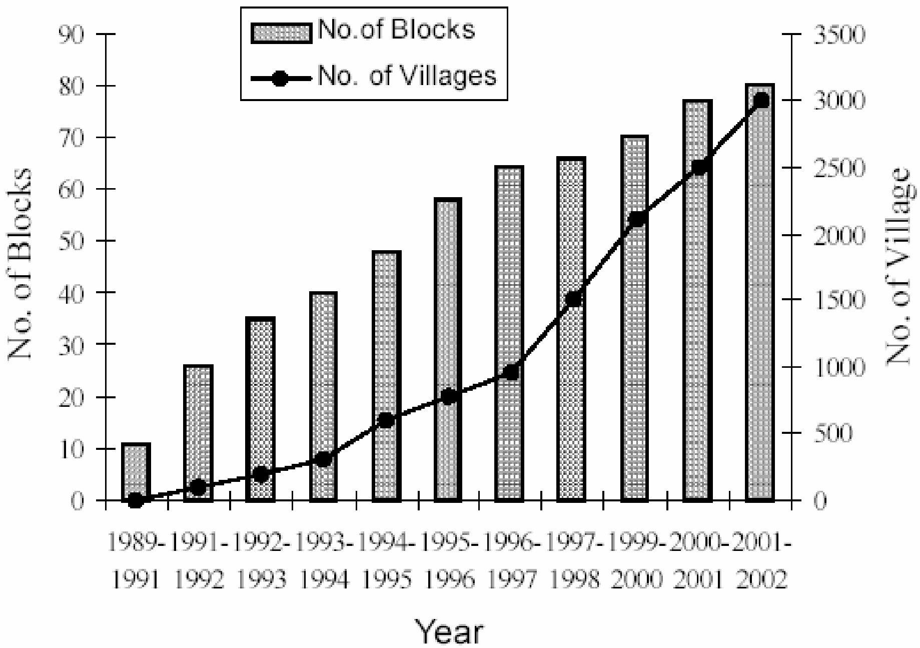

Fig. 1. Status of arsenic affected zones in West Bengal
Rys. 1. Ilość stref skażenie arsenem w Zachodnim Bengalu

5. Mechanism of mobilization

The occurrence, origin and mobility of both the contaminants in ground water are primarily influenced by local geology, hydrogeology and geochemistry of the sediment. Their presence in ground water may arise from the natural weathering and leaching of the respective rocks and minerals containing the elements, drainage from thermal springs and geysers as well as atmospheric depositions. The occurrence of fluoride is common in hot spring, but no such case has been reported for arsenic. The leaching of fluoride and arsenic depend on local condition viz, pH, temperature and the redox condition.

The parent minerals containing arsenic and fluoride and their alteration products are non-toxic as such. They are normally insoluble in water. Interestingly, the tube wells, dug wells and tanks located near the parent mineral deposits are not necessarily contaminated and the level of contaminants in many cases is quite within safe limit. The governing chemistry of contaminants (arsenic and fluoride) causing their elevated level in ground water is therefore plays an important role and the subject of interest.

a. Arsenic

Inorganic arsenic can occur in the environment in several oxidation states (III and V) and forms (inorganic and organic). Natural water contains mainly trivalent arsenite [As(III)] and/or pentavalent arsenate [As(V)]. Organic arsenic species, abundant in seafood, are very much less harmful to human health and are readily eliminated by the body. Iron arsenate ($FeAsO_4$) may be tentatively regarded as the direct and immediate source of arsenic because it is easily formed from Scorolite ($FeAsO_4$,$2H_2O$) and Pitticite (hydrated mixture of arsenate and sulphate) which are very common alteration products of Arsenopyrite (regarded as the primary mineral for arsenic). Since Arsenopyrite contains As^{3+} in small proportion with As^{5+} as the dominant constituent, it is quite likely that arsenic in the alluvium of Bengal Delta occurs as ferric arsenate ($FeAsO_4$) with ferric arsenite ($FeAsO_3$) in minor proportion. Under conditions of low pH and high Eh (redox potential) ferric arsenate, due to hydrolysis is dissociated (11) into arsenic acid (H_3AsO_4) whereas ferric arsenite breaks down into arsenious acid (H_3AsO_3). The relevant equations for such hydrolysis are as follows:

$$FeAs^{5+}O_4 \xleftrightarrow{3H_2O} H_3As^{5+}O_4 + Fe(OH)_3 \quad (1)$$

$$FeAs^{3+}O_3 \xleftrightarrow{3H_2O} H_3As^{3+}O_3 + Fe(OH)_3 \quad (2)$$

It is known that arsenic speciation and hence the mechanism of dissolution depend on pH and Eh. In acidic aqueous environment ferric hydroxide is soluble but it is precipitated in alkaline and reducing condition (at low Eh). So if the acidity of the solution decreases (pH increases) colloidal precipitation of ferric hydroxide should take place. Some As^{5+} and As^{3+} ions being absorbed on the particles of $Fe(OH)_3$ may be co-precipitated with the latter. This reduces arsenic content of water. However, precipitations of As^{5+} and As^{3+} are not simultaneous because As^{3+} is 5 to 10 times more soluble than As^{5+} and its stability in aqueous solution increases with the alkalinity of water and reducing character of the environment. Thus, even after colloidal precipitation of As^{5+} ions with ferric hydroxide the aqueous solution may contain As^{3+} ions in large amount.

b. Fluoride

Dissolution of fluoride species in natural water is controlled by Ca^{2+} ions and governed by thermodynamic principles. The $CaCO_3$ equilibrium in ground water plays an important role.

$$CaCO^3 + H^+ \leftrightarrow Ca^{2+} + HCO^{3-} \qquad (3)$$
$$K_{CaCO3} = [Ca^{2+}].[HCO^{3-}] / [H^+]$$

Similarly, the Fluorite equilibrium is:

$$CaF_2 \leftrightarrow Ca^{2+} + 2F^- \qquad (4)$$
$$K_{CaF2} = [Ca^{2+}].[F^-]^2$$

where K_{CaCO3} & K_{CaF2} indicate respective equilibrium constants and Due to hydrolysis […] indicate activity terms.

From equilibrium constant values of equations (3) & (4) therefore,

$$[F^-]^2 = [HCO^{3-}]. K_{CaF2} / [H+]. K_{CaCO3}$$

This indicates that at constant pH activity of fluoride ion is proportional to bicarbonate ion. Again, following the principle of ionic activity product, if the concentration of calcium and fluoride in natural water exceeds the solubility product of fluorite, CaF_2 precipitates (12).

6. Effects and pathophysiology

a. Arsenic

Chronic arsenic poisoning, as occurs after long-term exposure through drinking water is very different to acute poisoning. Immediate symptoms of an acute poisoning typically include vomiting, oesophageal and abdominal pain, and bloody ‘rice water’ diarrhea. Chelation therapy may be effective in acute poisoning but should not be used against long-term poisoning. The symptoms and signs appear to differ between individuals, population groups and geographic areas. Thus there is no universal definition of the disease caused by arsenic. This complicates the assessment of the burden on health of arsenic. Similarly, there is no method to identify those cases of internal cancer that were caused by arsenic from cancer induced by other factors. Long-term exposure to arsenic via drinking water causes cancer of the skin, lungs, urinary bladder and kidney, as well as other skin changes such as pigmentation changes and thickening (hyperkeratosis). Absorption of arsenic through the skin is minimal and thus hand-washing, bathing, laundry etc. with water containing arsenic do not pose human health risk. Following long-term exposure, the first changes are usually observed in the skin. Cancer is a late phenomenon, and usually takes more than 10 years to develop. Some studies have reported hypertensive and cardiovascular disease, diabetes and reproductive effects (13). Exposure to arsenic via drinking water has been shown to cause a severe disease of blood vessels leading to gangrene to China (Province of Taiwan), known as ‘black foot disease’.

Pathophysiology

Inorganic forms of arsenic are more toxic than organic forms. The trivalent forms are more toxic and react with thiol groups, while the pentavalent forms are less toxic but uncouple oxidative phosphorylation. Very few organ systems escape the toxic effects of arsenic (1). Trivalent inorganic arsenic inhibits pyruvate dehydrogenase by binding to the sulfhydryl groups of dihydrolipoamide. Consequently conversion of pyruvate to acetyl coenzymeA (CoA) is decreased, citric and cycle activity is decreased, and production of cellular ATP is decreased. Trivalent arsenic inhibits cellular glucose uptake, gluconeogenesis, fatty acid oxidation, and further production of acetyl CoA. It also blocks the production of glutathione, which prevents cellular oxidative damage.

Effects of pentavalent inorganic arsenic occur partially because of its transformation to trivalent arsenic; toxicity proceeds as outlined above. More importantly, pentavalent arsenic resembles inorganic phosphate and substitutes for phosphate in glycolytic and cellular respiration pathways. High-energy phosphate bonds are not made, and uncoupling of oxidative phosphorylation occurs. In the presence of pentavalent arsenic, adenosine diphosphate (ADP) forms ADP-arsenate instead of ATP; the high-energy phosphate bonds of ATP are lost (14).

b. Fluoride

Fluoride was first used to fight dental cavities in the 1940's, the effectiveness depended on the grounds that (i) fluoride inhibits enzymes that breed acid producing oral bacteria whose acid eats away tooth enamel and (ii) fluoride ions bind with calcium ions, strengthening tooth enamel as it forms in children. Researchers now consider this more of an assumption than fact and it is now universal that fluoride intake have detrimental effects on health i.e, the incurable fluorosis. Aches and pain in the joints, viz. neck, back, hip, shoulder and knee without visible signs of fluid accumulation, may be due to fluoride toxicity manifestations besides other reasons. Non-ulcer dyspepsia, viz. nausea, vomiting, pain in the stomach, bloated feelings/gas formation in the stomach, constipation followed by diarrhea may be due to fluoride toxicity (15). Polyurea (tendency to urinate more frequently) and polydipsia (excessive thirst) is common symptom of fluoride toxicity besides diabetes. Muscle weakness, fatigue, anemia with very low hemoglobin levels may also occur. Complaints of repeated abortions/stillbirth as well as male infertility with abnormality in sperm morphology, oligospermia (deficiency of spermatozoa in the semen), azoospermia (absence of spermatozoa in the semen) and low testosterone levels are also repoted (16). Any discoloration of the enamel surface, in front row of teeth of the patient (central and lateral incisors of the upper and lower jaw) may be due to dental fluorosis.

Pathophysiology

Excess fluoride affects calcium functioning, which is most essential for bone formation as well as for muscle movement. As fluoride binds with calcium, less calcium is available for normal body functioning. Calcium needed for blood clotting and every muscular contraction becomes less. Constant dysfunction of muscular contraction leads to the typical knock-knee symptom. Excess accumulation of calcium fluoride in the renal system lead to stone formation in the kidney and eventual renal failure. The living mucosa of the gastro intestinal system is destroyed by the fluoride. There are reports that fluoride may interact synergistically with other environmental pollutants to produce greater effects than either pollutant could cause were it acting alone (2). Pronounced synergistic effects between fluoride and copper; hydrogen fluoride and sulphur dioxide in air are reported.

7. Health status of people: case study

In a typical study, around 21,000 hair, nail, skin-scale and urine (only arsenic metabolites were measured) samples were analyzed for arsenic from the villagers in the area where arsenic patients were found (17). The result is presented in Table 1. About 10÷15% of these samples analyzed are from people having arsenical skin lesions. But the analytical report shows that 56%, 80% and 87% of the analyzed samples have arsenic in hair, nail and urine above normal/toxic level (hair), respectively. [Normal level of arsenic in hair ranges from 80÷250 µg/kg; 1000 µg/kg is the indication of toxicity. Normal range of arsenic in nail is from 430÷1080 µg/kg; in urine from 5÷40 µg/L (per day)]. During the dermatological survey in the affected villages it was observed that often 30÷40% population drinking the same arsenic contaminated water, may not show arsenical skin lesions, but their hair, nail and urine contain high concentration of arsenic. Thus many of the villagers may not be showing arsenical skin lesions, but there is a possibility that they are sub-clinically affected.

Table 1. Concentration of arsenic in hair, nail, urine (metabolites) and skin-scale collected from typical arsenic affected area in West Bengal
Tabela 1. Stężenia arsenu we włosach, paznokciach, moczu (metabolity) i naskórku zebrane na typowym terenie skażonym arsenem w Zachodnim Bengalu

Parameters	No. of observation	% of samples having arsenic above normal level
As in hair	6286	56
As in nail	6413	80
As in urine	8397	87
As in skin-scale	62	–

Our study in the village Nashipur, Bhabanandapur, Nowapara, Chakatla, Junidpur in the Rampurhat block of district Birbhum, West Bengal, India reveal a maximum fluoride concentration of 16.0 mg/L (almost 16 times higher than permissible limit by WHO). In the present study area almost 90% of the children below age group of 15 years are developed the symptom of dental fluorosis. Instead of bright smooth teeth, dull teeth with yellow spot, brown stain, pitting and chipped off edges are very known. The harmful effect of fluoride on the teeth is believed to be cumulative with respect to duration, level of fluoride exposure and maturity stage of teeth enamel. The damage is higher during matrix forming secretary stage of enamel rather than in rapidly mineralizing maturation stage. We found 60% of the subjects in the study area are affected with dental lesion. The dental damage is categorized as G1-G4 as per Teotia and Teotia (18). Only 10% of the subjects are detected free from dental problem. The relative proportion of damage in male and female child is present in figure 2. The biochemical and scanning electron microscopic studies indicate an increase in fluoride content in their teeth. Above 60% of the adult are developed the symptom of skeletal fluorosis. The radiological studies show the development of Kyphosis of the dorsal spine and stiffness of the neck. Statistics revealed that out of 152 patients 99 complained of backache and 81 of them had mild to severe dorsolumbar Kyphosis and limitation of spinal movement. Simultaneously the great joints like hips, knees, shoulders and elbows were stiff and deformed in 29 cases who experienced lot of difficulties in their daily day activities such as walking, sitting on the ground, forward bending, kneeling and hand to mouth movement. Four patients with severe Kyphotic spine were having respiratory distress on slight exertion because of rigid chest wall. Respiration in those cases was almost abdominal type. The cattle in these areas show the symptom of skeletal fluorosis, which results probably due to consumption of fluoride rich water and contaminated grass.

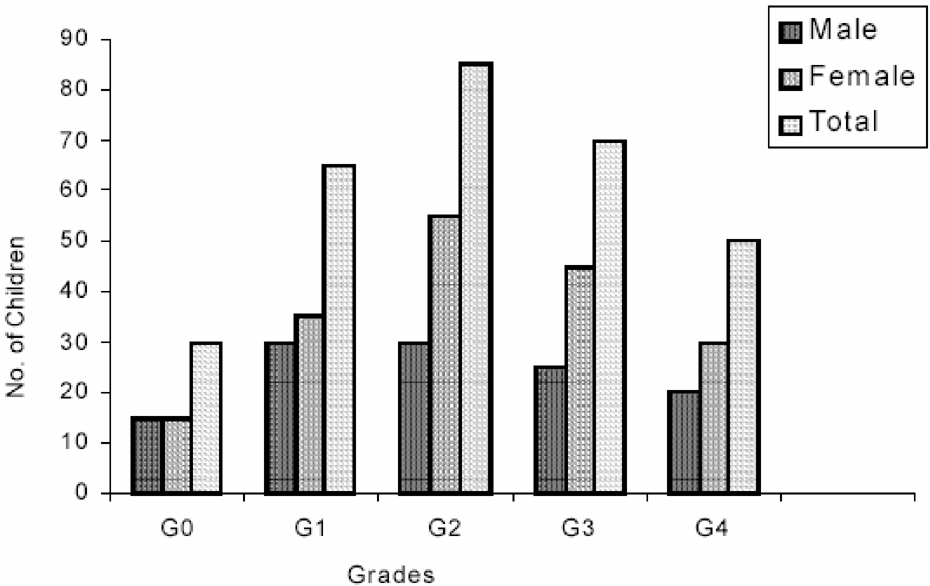

Fig. 2. Dental fluorosis among children below 16 years in Birbhum district of West Bengal

Rys. 2. Fluoroza zębów u dzieci poniżej 16 roku życia w okręgu Birbhum Bengal Zachodni

8. Management of the problem

Identification of water sources

A thorough survey and detailed investigation on the water quality of all drinking water sources is highly needed. The sources should be marked as safe, contaminated or unsafe. Only the safe sources are recommended for consumption as drinking and irrigation. The moderately contaminated sources are meant for other purposes and the unsafe sources should be rejected. Frequent monitoring and management of all the drinking water sources is necessary.

Awareness programme

Awareness for arsenic and fluoride toxicity among the people is highly required so that they may consume water only from safe sources. At the same time from the information of geochemical aspects, rainfall terrain and population, digging of tube well from safe aquifer is needed. People should be encouraged for dual system of water usage. Regular health survey together with intake of calcium, Vitamin C, E and antioxidant containing foods may minimize harmful effects.

Remedial Process

Fluoride and Arsenic poisoning can be prevented or at least minimized by use of alternative water sources and treated water after removal of fluoride and arsenic.

Surface water, rainwater and fluoride/arsenic free ground water can be considered as alternative water sources. Among the conventional removal techniques precipitation, adsorption, ion exchange, electrolysis and reverse osmosis can be used. In our laboratory we tested some low cost waste material (viz. fly ash from thermal power plant) and natural material (laterite, the widely available clay in India) for the removal of arsenic and fluoride from contaminated drinking water.

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Wpływ geośrodowiskowych zagrożeń na wody gruntowe i zdrowie ludzkie: mechanizm i zarządzanie

Streszczenie

Ostatnie sprawozdania pokazują, że około 26 krajów jest dotkniętych problemem zanieczyszczenia wód gruntowych arsenem, wśród których cztery kraje południowo azjatyckie: Bangladesz, Indie (Zachodni Bengal), Chiny i Tajwan są najbardziej zagrożone. Obecnie w 29 krajach na świecie występuje problem zanieczyszczenia wód gruntowych fluorem pochodzącym tylko ze źródeł geośrodowiskowych. Wpływ na zdrowie przypadku obu tych zanieczyszczeń jest bardzo poważny, a skutki są nieodwracalne i praktycznie nie istnieje żadna kuracji mogąca wyleczyć zakażone osoby.

W Indiach bardzo duża populacja cierpi z powodu zatrucia arsenem i fluorem. Ostatnie badania przeprowadzone przez UNICEF wskazują, że co najmniej 213 okręgów w 18 stanach (w tym cztery okręgi Zachodniego Bengalu), jest dotknięte tym problemem. Skala problemu zanieczyszczenia arsenem w Zachodnim Bengalu jest bardzo poważna w dziewięciu okręgach z pośród osiemnastu. Średnia wysokiego stężenia arsenu jest 4,5 razy przekracza wartość tolerowaną przez ludzkie ciało (0,05 mg/L, norma w Indiach). W niektórych miejscach wartość ta przekroczona jest nawet siedmiokrotnie. Najwyższe oznaczone stężenie fluoru w wodzie gruntowej w Zachodnim Bengalu wynosiło 19 mg/L (maksymalna dopuszczalna wartość wg WHO to 0,5 mg/). Największe stężenie fluoru w wodzie gruntowej w Indiach oznaczono w miejscowości Haryana i wynosiło ponad 84 mg/L.

Nasze badania we wsiach Nashipur, Bhabanandapur, Nowapara, Chakatla, Junidpur w dzielnicy Rampurhat, okręgu Birbhum, Zachodni Bengal pokazują największe stężenie fluoru wynoszące 16,0 mg/L (prawie 16 razy większe niż granicę dopuszczalną przez WHO). Na terenie badań prawie 90% dzieci w grupie wiekowej poniżej 15 lat posiada rozwinięte symptom fluorozy dentystycznej. W typowych badaniach około 21 000 próbek włosów, paznokci, naskórka i moczu (tylko metabolity arsenu zostały zmierzone) mieszkańców terenów skażonych arsenem zostało zanalizowanych na zawartość arsenu. Około 10÷15% z tych próbek pochodzi od ludzi mających uszkodzenia skóry spowodowane przez arsen. 56%, 80% i 87% z analizowanych próbek zawiera arsen we włosach, paznokciach i moczu w ilościach przekraczających poziom normalnym / toksyczny (włosy).