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Chapter 4

Ground Water Contamination with Fluoride and Potential Fluoride Removal Technologies for East and Southern Africa

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Additional information is available at the end of the chapter

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1. Introduction

Ground water is main source of water supply in most rural communities in Africa. It has good microbiological and biological properties in general as such requires minimal treatment. Unfortunately groundwater is sometimes contaminated with naturally occurring chemicals. One such naturally occurring toxicant is fluoride. In some parts of Africa ground water contains high fluoride levels beyond the recommended World Health Organisation upper limit of 1.5 mg/l. It is reported that the East African Rift Valley is a high fluoride area. This region extends from Jordan valley down through Sudan, Ethiopia, Uganda, Kenya and Tanzania. High fluoride levels have also been reported in Malawi and The Republic of South Africa. In Kenya high fluoride levels in ground water beyond 5 mg/l and beyond 8 mg/l were reported in 20% and 30% respectively of 1000 samples taken nationally. A survey of fluoride in ground water in Tanzania showed that 30% of the waters used for drinking exceeded 1.5 mg/l fluoride. In Malawi and the Republic of South Africa fluoride levels beyond 1.5 mg/l and occurrence of dental fluorosis have also been reported. Proxy indicators of high fluoride levels in ground water are high pH, pH beyond 7, and high sodium and bicarbonate concentrations in the water. High fluoride waters often have low calcium and magnesium concentrations as such are fairly soft. There are some exceptions of fluoride occurrence that may not adhere to these proxy indicators.

The beneficial effects of ingesting fluoride to human health are limited to fluoride levels approaching 1.0 mg/l in potable water. It is reported that drinking of water with such levels of fluoride improves skeletal and dental health. Ingestion of water with fluoride levels beyond 1.5 mg/l has negative health impacts. Amounts in potable water between 1.5 and 3.0 mg/l will cause browning and mottling of teeth referred to as dental fluorosis. This is the onset of

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fluorosis that makes the teeth very hard and brittle. Concentrations between 4 to 8 mg/l result in skeletal fluorosis and crippling fluorosis ensues when water of greater than 10 mg/l fluoride is ingested for a prolonged period of time. Skeletal fluorosis is characterized by bone malformation resulting in movement difficulties while crippling fluorosis is characterized by weakening of the bones, and bone junctions growing together causing immobility. Excessive fluoride ingestion has other health effects reported in literature, among which are muscle fibre degeneration, low haemoglobin levels, red blood cell deformities, excessive thirst, headache, skin rashes, depression, gastrointestinal problems, urinary tract malfunction, nausea, abdominal pains, tingling sensation in fingers and toes, reduced immunity and neurological manifestations similar to pathological changes that occur in Alzheimer's disease patients. These effects have received less attention compared to dental and skeletal fluorosis that are typical in high fluoride areas.

Ingestion of fluoride through food and air is relatively small compared to fluoride ingestion through water. Attention has thus been drawn to controlling fluoride concentrations in water supplied for drinking. The World Health Organisation recommends that in mitigating for fluorosis in endemic areas the approach should be hierarchical in the following order; first to identify alternative source of potable water with low fluoride content, secondly to dilute high fluoride water with low fluoride water to attain a mass balance of within 1.5 mg/l, thirdly to use high calcium, magnesium and vitamin c diets and finally, when all these may not be feasible; to remove fluoride from water to meet the required level of 1.5 mg/l. Water defluoridation, the removal of fluoride from water, has been studied widely in time, space and materials. This is because the other lines of interventions are often not plausible in high fluoride rural areas where natural sources of water are used and income levels are humble. Wide research has resulted in an a lot of data and information on water defluoridation that may be employed in deciding for fluoride removal techniques at household, communal, municipal or regional level. However this information is oftentimes in different source materials and in different formats.

This chapter aims at enhancing progress towards access to safe drinking water through consolidating knowledge in groundwater fluoride occurrence, effects of fluoride on human health, and technologies available for water defluoridation in East and Southern Africa. Specifically the chapter will; provide information on fluoride occurrence in Eastern and Southern Africa and respective health effects to guide choices and decisions in water supply and treatment at municipal, regional and national level; consolidate research findings in water fluoride and defluoridation science for scientists and non-scientists that will assist in choices of water defluoridation technologies at home or local community and; exemplify research in special water treatment technologies through water defluoridation science for students in water resource sciences. To meet these objectives the chapter is outlined as follows;

2. Fluoride and human health

The beneficial and harmful effects of fluoride ingestion are separated by a very narrow margin. Fluoride ingestion through potable water with concentrations about 1.0 mg/l is known to

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strengthen teeth and the skeleton; however water concentrations beyond 1.0 mg/l are undesirable because prolonged consumption of such water causes fluorosis. Dental fluorosis is caused by prolonged consumption of water with fluoride concentrations between 1.5 and 4.0 mg/l. This is characterised by browning and mottling of teeth. Prolonged drinking of water with concentrations of fluoride between 4.0 and 10 mg/l causes skeletal fluorosis and when water of concentrations beyond 10.0 mg/l is taken for a long time crippling fluorosis may ensue [1]. Skeletal fluorosis is characterised by weakening of bones and malformation of the skeleton. Symptoms of crippling fluorosis are the growing together of bone junctions causing immobility. The science behind the beneficial and harmful effects of fluoride on the skeletal structure is based on the possible ion exchange reactions between hydroxide and fluoride ions in the calcium hydroxy-phosphate, the main skeletal structure compositional material. The replacement of hydroxide ions with fluoride ions, Equation 1, results in a more acid resistant structure, fluoroapatite.

$$Ca_5(PO_4)_3OH + F^- \rightarrow Ca_5(PO_4)_3F + OH^- \tag{1}$$

Fluoroapatite being more resistant to acid attack compared to hydroxyapatite offers a protective layer to the tooth enamel against acids from foods. This prevents dental caries. Excessive fluoride intake however may enhance the reaction to go beyond replacement of hydroxide, Equation 2.

$$Ca_5(PO_4)_3F + 9F^- \rightarrow Ca_5F_{10} + 3PO_4^{3-} \tag{2}$$

In Equation 2 ion exchange occurs between phosphate and fluoride ions. The resultant compound, calcium decafluoride, is a very hard and brittle material not appropriately suited for the functions of the skeletal structure [2]. Other complications associated with excessive consumption of fluoride are muscle degeneration, low heamoglobin content, deformities of red blood cells, skin rashes, depression, abdominal pains, urinary tract malfunction, reduced immunity, tingling sensation in fingers and toes, excessive thirst, and, neurological manifestations similar to pathological changes that occur in Alzhemer's disease patients [3]. Dental and skeletal fluorosis has however attracted greater attention as compared to the other effects of fluoride because of its obvious manifestations. In Malawi for instance, high correlation was obtained between levels of fluoride in drinking water with occurrence of dental fluorosis in primary school pupils. High correlation between fluoride levels in groundwater and occurrence of dental fluorosis was also obtained in a number of districts in the country. Significant correlation ($r^2 = 0.77$) between levels of fluoride in borehole water and manifestation of dental fluorosis in primary school pupils of Liwonde, a township in Southern Malawi. A similar picture emerges in Nathenje, a township in Central Malawi, where 68.5 % of school going children in high fluoride areas showed signs of dental fluorosis [4, 5].

Incidences of fluorosis have been reported in the Republic of South Africa in high fluoride areas. Research has shown that 803 areas are fluorosis endemic in South Africa. These areas

include locations in Western and Karoo Regions of Cape Province, the North Western, Northern, Eastern and Western areas of Transvaal, Western and Central Free State. A study on dental fluorosis occurrence among children revealed that even at low concentrations of fluoride in potable water dental fluorosis ensues. In sub optimal fluoride areas (0.4 – 0.6 mg/l) dental fluorosis was evidenced in about 19 % of children [3]. Results obtained, illustrate that there may be no universal safe levels of fluoride in drinking water [6]. Significant dental fluorosis incidences were noted in low, medium and high fluoride areas, Table 1.

Location	Fluoride concentration in potable water	% with Dean's index score greater than 2.
Sanddrif	0.19	47
Kuboes	0.48	50
Leeu Gamka	3.0	95

Table 1. Fluoride and dental fluorosis occurrence in three locations of South Africa; [3, 6]

Much higher fluoride levels occur in Tanzania and high dental and skeletal fluorosis have been reported in the Kilimanjaro region. Among 119 children aged between 9 and 13 severe dental fluorosis was evident in 87.4 % of the children at Maji ya chai in Meru, Tanzania. These children had lived all their lives within this area and drank water from a river with fluoride levels of 18.6 mg/l. Very high occurrence of dental fluorosis was also reported among adults in Arusha, 83 %, and in Moshi, 95 %, in Tanzania. Regions most affected in Tanzania are Arusha, Moshi, Singida and Shinyanga. In Arusha skeletal fluorosis has been observed [3, 7].

Dental fluorosis in Kenya has been reported as having a prevalence rate of up to 39.6 % in three racial groups. Table 2 illustrates the distribution of signs of dental fluorosis classified using the extent of affliction;

Distribution of dental fluorosis (%) ⇩	Race ⇨ African	Asian	European
Sample size	3,014	626	922
Normal	46.4	30.4	61.3
Questionable	15.7	11.7	15.7
Very mild	17.9	17.5	13.4
Mild	10.8	28.6	6.4
Moderate	5.5	5.7	2.3
Severe	3.7	6.1	0.9
Prevalence (%)	37.9	57.9	23.0

Table 2. Reported prevalence of dental fluorosis in Kenya; [8]

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Areas most affected in Kenya are the Northern Frontier (Turkana), Northe-West Kenya, Southern Rift Valley, Central and Eastern Regions. Surveys found that 67 % of Asian, 47 % of African and 30 % of European school children showed signs of dental fluorosis of varying degree. The high prevalence in Asian population was speculated to relate to their vegetarian diet [3]. This research carried out in Kenya employed Dean's index that is decribed below.

Class	Description
1. Normal	Complete absence of any white flecks or white spots
2. Questionable	A few white flecks to occasional white spots.
3. Very mild	Less than 25 per cent of the tooth surfaces covered by small white opaque areas
4. Mild	Fifty per cent of the tooth surfaces covered by white opaque areas.
5. Moderate	Nearly all the tooth surfaces are involved, with minute pitting and brown or yellowish stains.
6. Severe	Smoky white appearance of all the teeth with hypoplasia, chipping and large brown stains, which vary from chocolate brown to black. There is discreet and confluent pitting, often accompanied by attrition.

Table 3. Dean's Index; [9]

There are other indices that are often employed. These are; DDE (Developmental Defects of Enamel) index developed by Federation Dentaire Internationale in 1992; Thylstrup Fejerskov (TF) index by Thylstrup and Fejerskov (1978) and Tooth Surface Index of Fluorosis (TSIF) developed by Horowitz et al., in 1984 [3].

Annual average of maximum daily air temperature (°C)	Recommended fluoride concentration (mg/l)			Maximum allowable fluoride concentration (mg/l)
	Lower	Optimum	Upper	
10 – 12	0.9	1.2	1.7	2.4
12.1 – 14.6	0.8	1.1	1.5	2.2
14.7 – 17.7	0.8	1.0	1.3	2.0
17.8 – 21.4	0.7	0.9	1.2	1.8
21.5 – 26.2	0.7	0.8	1.0	1.6
26.3 – 32.5	0.6	0.7	0.8	1.4

Table 4. USPHS Fluoride recommendations in drinking water

Many parts of some countries in Africa are also affected by fluorosis. These include some areas in Sudan, Uganda, Ethiopia, Senegal and Niger. Fluoride ingestion is highly linked to drinking water because the contributions from other sources, such as food and air is minimal. The United States Public Health Service [10] set some guidelines for lower, optimal, upper and maximum allowable fluoride concentrations in drinking water with respect to average air temperature, Table 3:

3. Fluoride occurrence in the world

Geogenic occurrence of fluoride is often linked to volcanic activity, fumaric gases and presence of thermal waters. Proxy indicators of high fluoride levels in groundwater are; low levels of calcium and magnesium, high levels of sodium and bicarbonate ions, and high pH above 7. There are however some exceptions to these generic conditions [11]. High fluoride ground waters are typically of sodium chloride, or sodium chloride bicarbonate type characterised by high pH. Areas with high fluoride in ground water include fluoride beds encompassing parts of Iraq, Iran, Syria, Turkey, Algeria and Morocco, and the East African rift system extending from Jordan valley down through Sudan, Ethiopia, Uganda, Kenya and Tanzania. There are high fluoride areas in other parts of the world, Figures 1 to 6 show high fluoride areas of the world.

Fluoride is found in a wide variety of minerals that include fluorspar (CaF_2), cryolite (Na_3AlF_6), apatite ($Ca_5(PO_4)_3F$) and hornblende [$(ca,\ Na)_2(Mg,\ F,\ Al)_5(Si,\ Al)_8O_{22}(OH)_2$]. The average crustal abundance is known to be about 300 mg/kg representing between 0.06 to

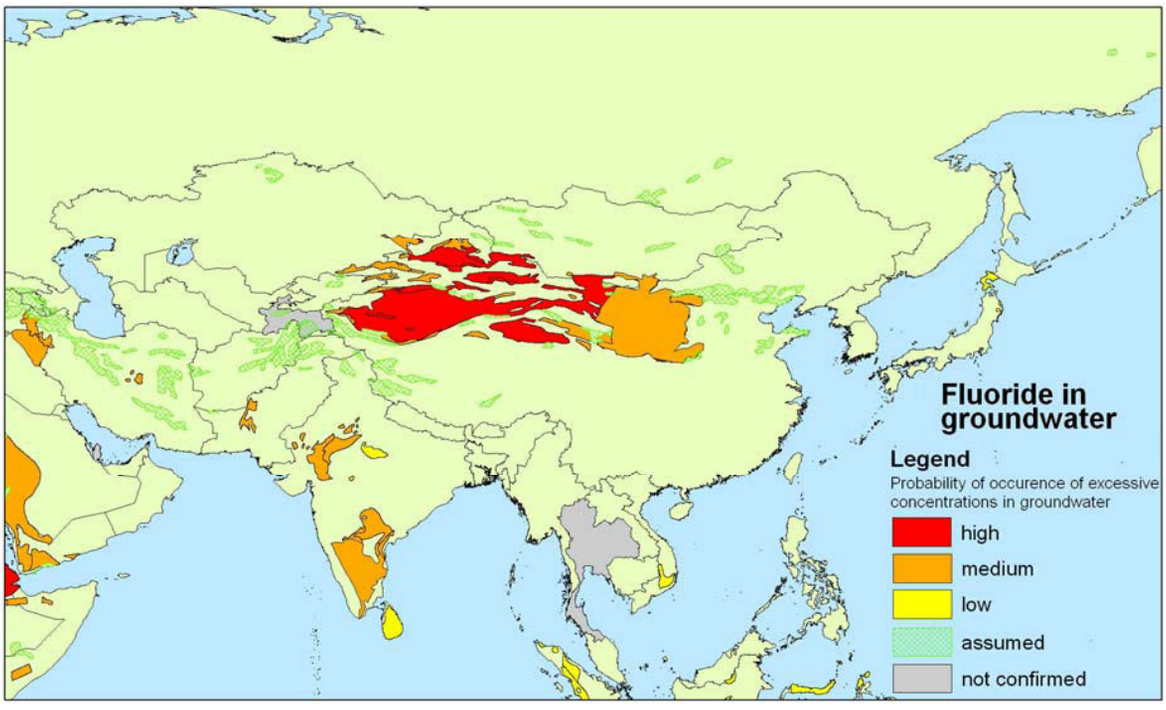


Figure 1. Fluoride occurrence in groundwater in Asia [11]

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0.09 % by weight of the earth crust. The presence of fluoride in ground water results from dissolution of fluoride bearing minerals where the water is in contact with a fluoritic bed.

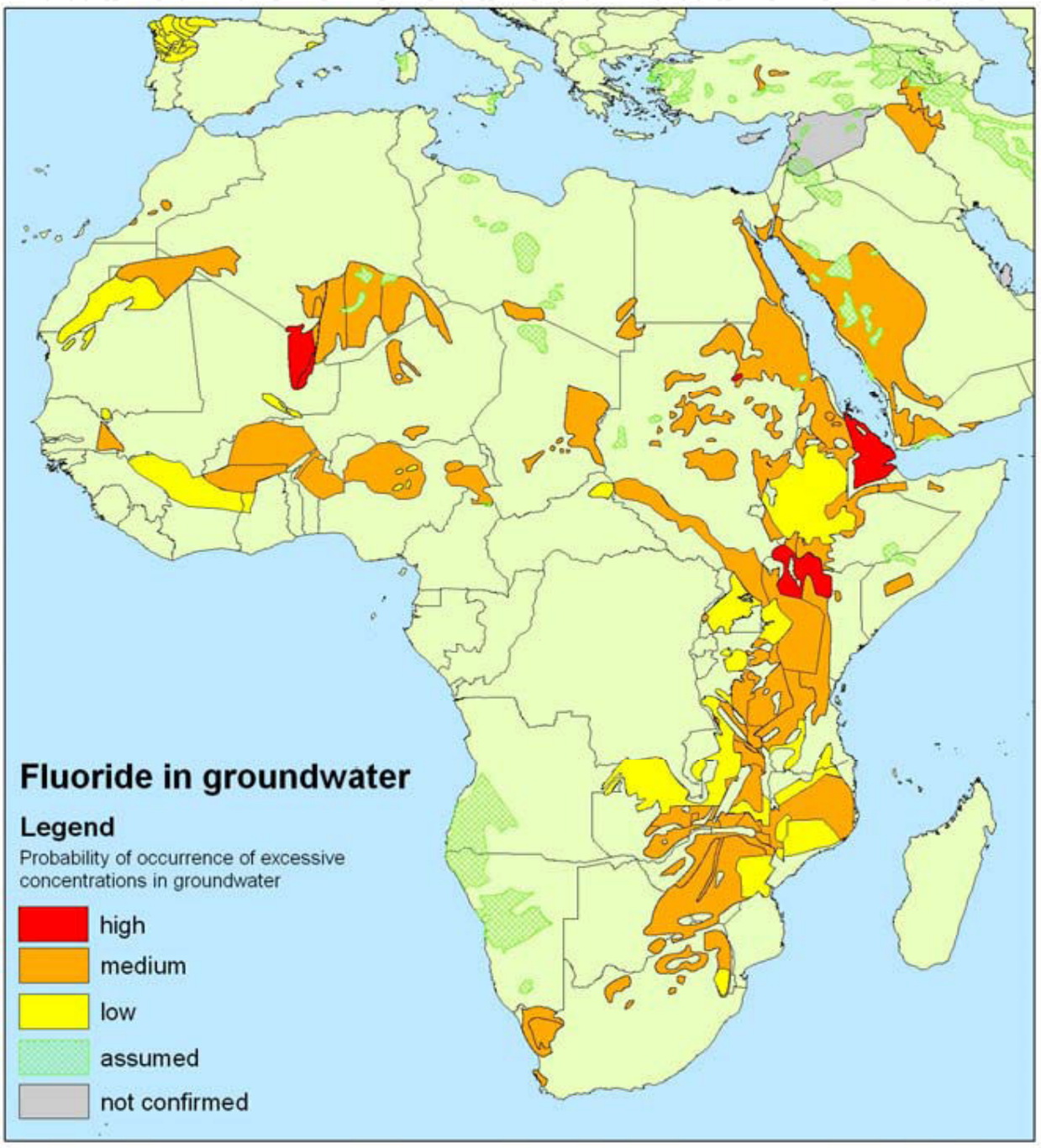


Figure 2. Fluoride occurrence in groundwater in Africa [11]

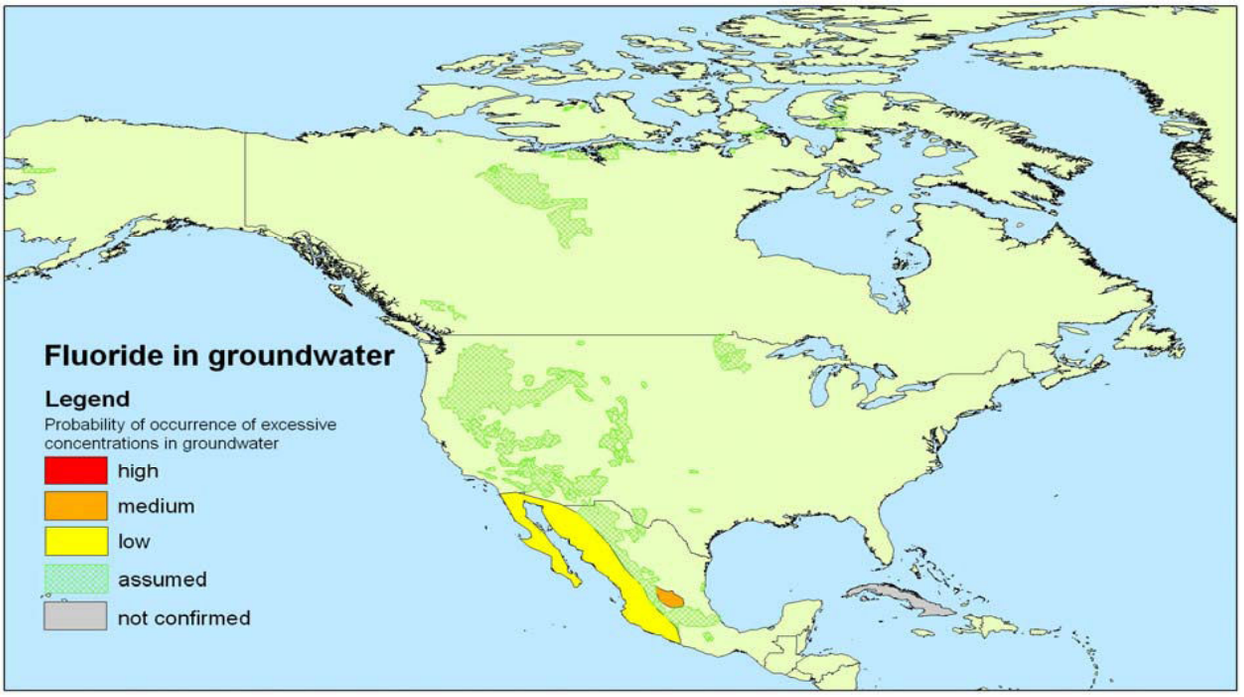


Figure 3. Fluoride occurrence in groundwater in North and Central America [11]

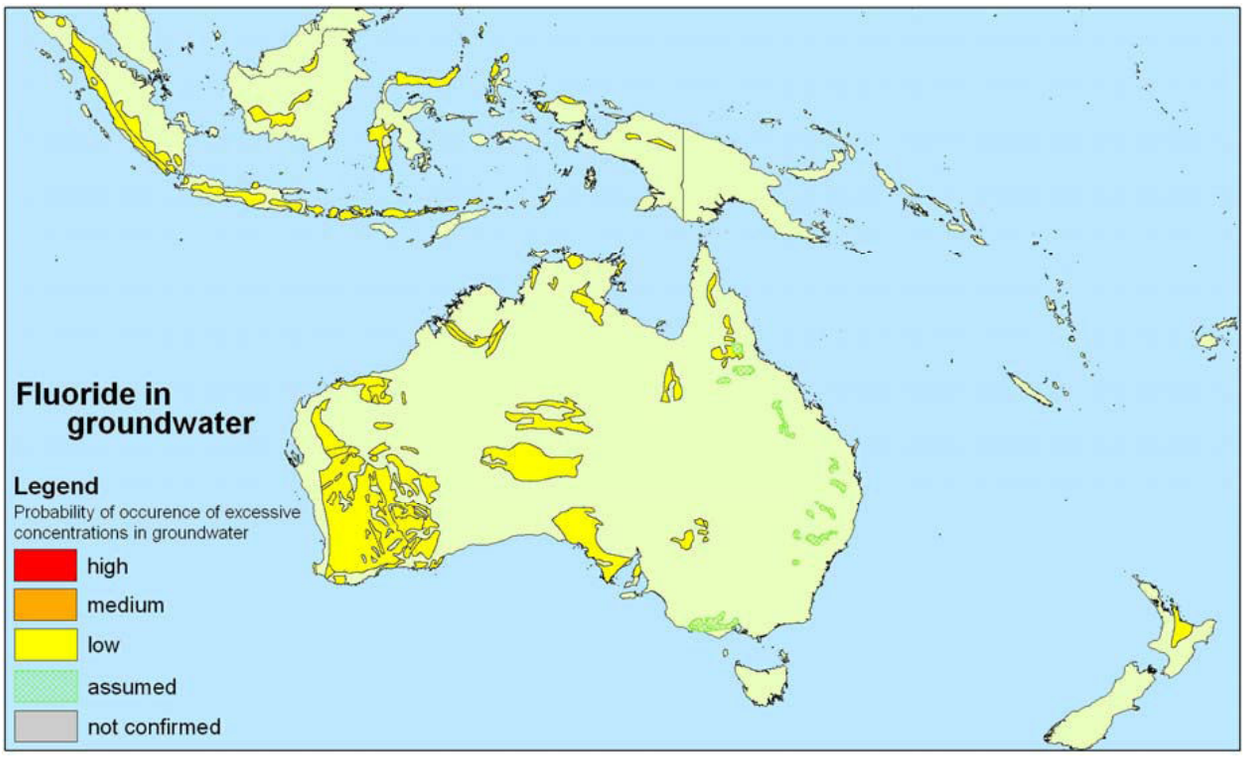


Figure 4. Fluoride occurrence in groundwater in Oceania [11]

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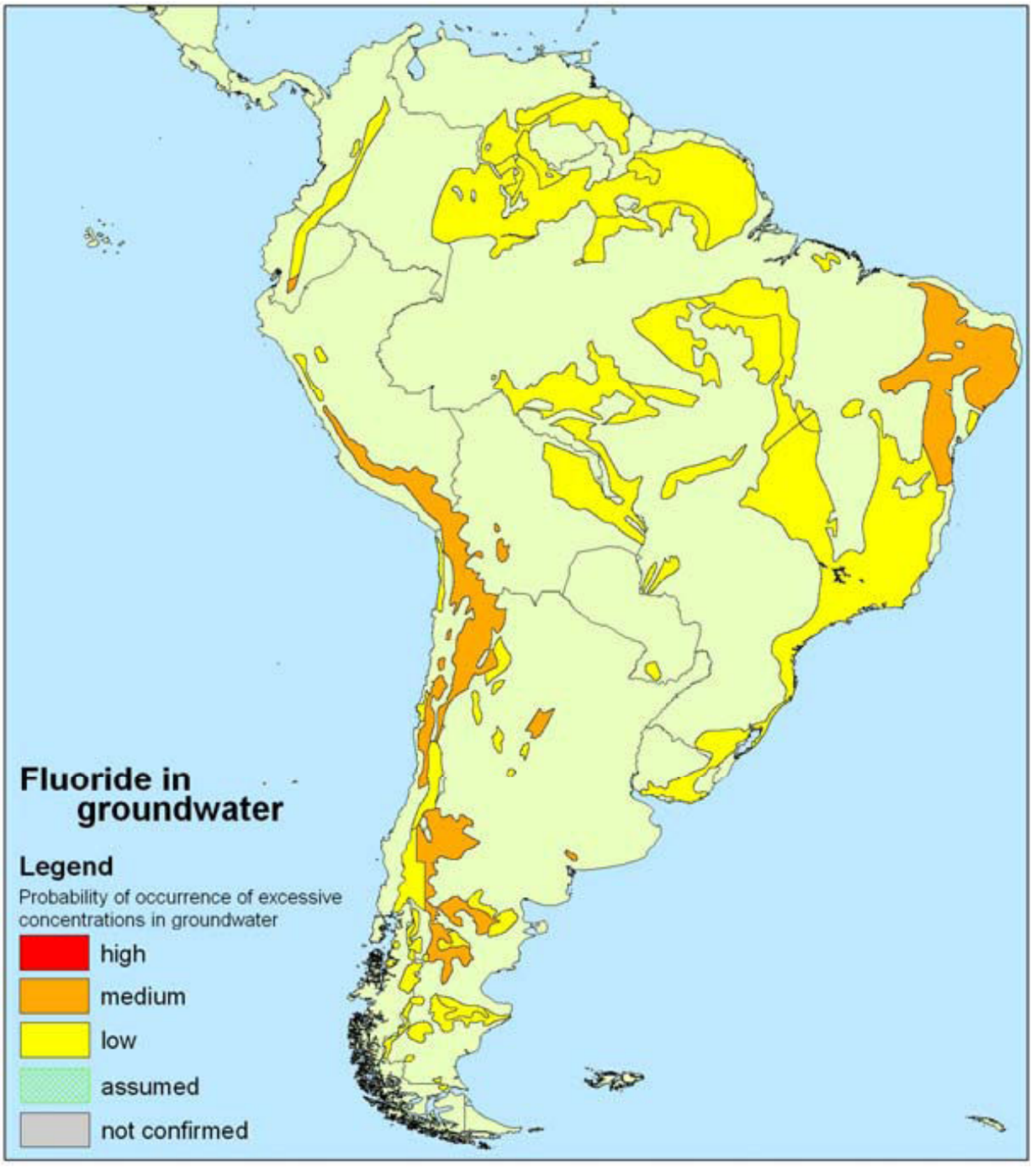


Figure 5. Fluoride occurrence in groundwater in South America [11]

4. Fluoride occurrence in East and Southern Africa

High fluoride levels occur in ground waters in some parts of Kenya, Tanzania, Malawi and The Republic of South Africa; however the East African countries have higher levels compared

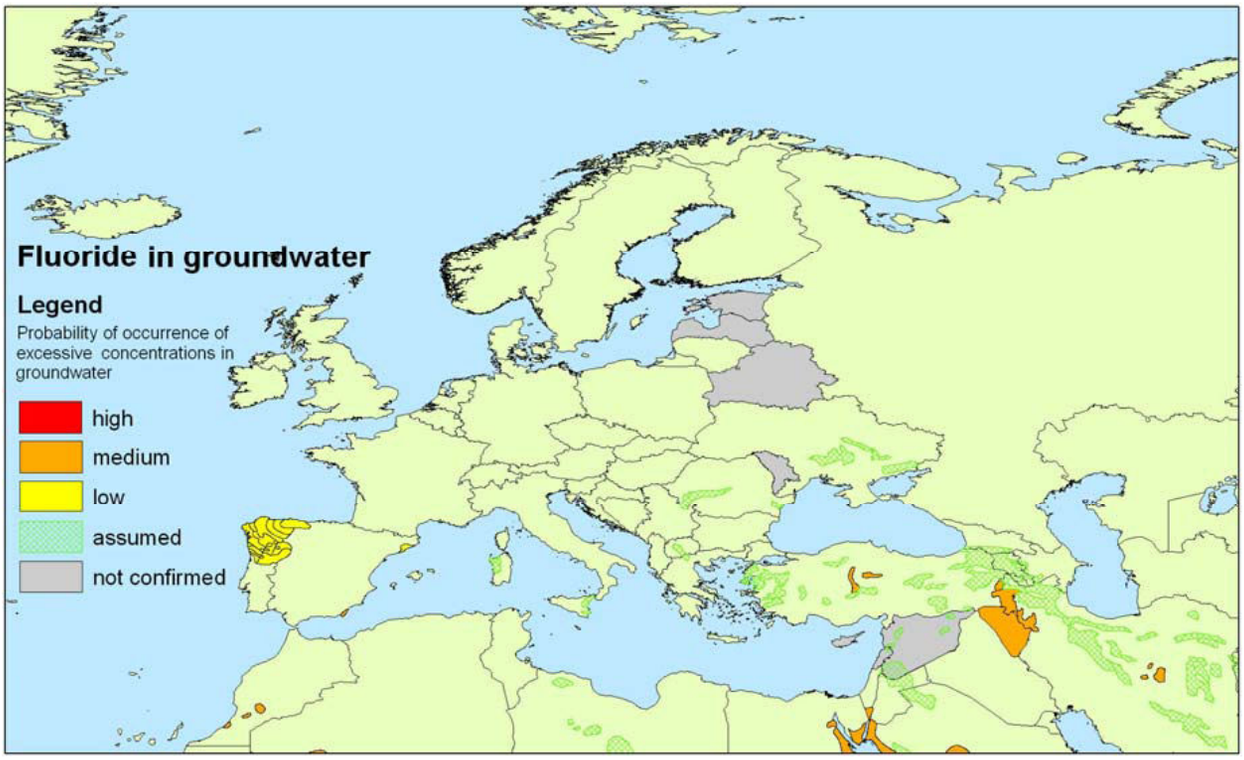


Figure 6. Fluoride occurrence in groundwater in Europe [11]

Location	Average fluoride level in ground water
Arusha Maji ya Chai, Arumeru District	20.0
Lemongo spring 10.5	10.5
Kikati B/H 113/79 11.0	11.0
Masai Furrow- Tingatinga 32.0	32.0
B/H 186/81 - Hanang 46.0	46.0
Singida S/W 8/78 - Ngorongoro 11.6	11.6
Senene 10.5	10.5
Well camp Doromoni 21.3	21.3
Fish camp Migilango village 12.5	12.5
Hot spring - Manyoni 10.5	10.5
Shinyanga S/W Mkokolo 17.0	17.0

Sourced from Ngurdoto Defluoridation Research Centre, Tanzania

Table 5. Fluoride concentrations in some ground water sources in Northern Tanzania

to the Southern Countries. In Tanzania for example, fluoride concentrations in ground water of up to 40 mg/l have been reported, see Table 5. Some lakes in East Africa have extremely high fluoride concentrations, an occurrence not typical in surface waters. Lake Elmentaita and Lake Nakuru of Kenya have fluoride concentrations of 1,640 mg l–1 and 2,800 mg l–1 respectively [12]. The Tanzanian Lake Momella is reported to have a fluoride concentration of 690 mg/l [3].

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A detailed survey of fluoride concentrations carried out in Kenya revealed that 20 % of the samples had fluoride levels greater than 5 mg/l and 12 % of the samples exceeded 8 mg/l. A total of 1000 samples were taken from different locations covering the whole country. The highest concentrations were reported in ground waters of the volcanic areas of the Nairobi, Rift Valley and Central Provinces where maximum groundwater fluoride concentrations were as high as 30–50 mg/l [12]. In Tanzania concentrations of up to 45 mg/l have been detected in the rift valley. The most affected areas of Tanzania are Mwanza, Mara, Shinyanga, Arusha, Kilimanjaro and Singida shown in shaded lines in Figure 7.

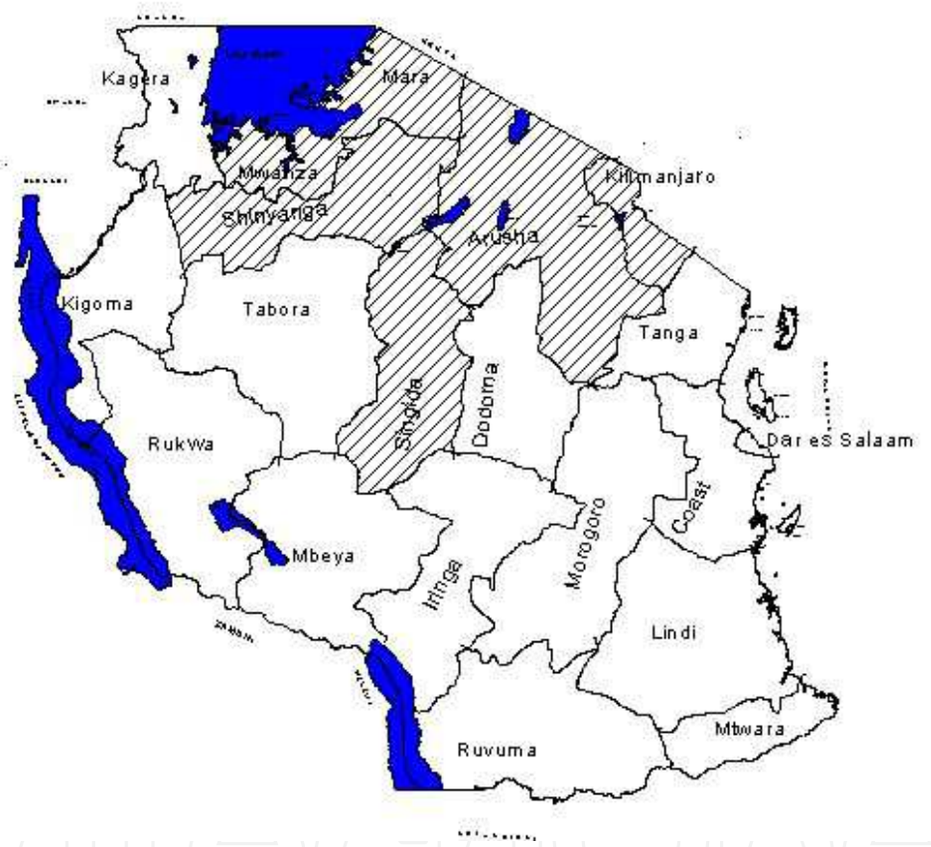


Figure 7. Map of Tanzania showing areas most affceted with fluoride (Sourced from Ngurdoto Defluoridation Research Station)

Fluoride occurrence in groundwater in Malawi has been better surveyed in the southern region [13, 14, 15]. Some data extracted from research is depicted in Table 6.

Research in the Republic of South Africa has shown that underground mine waters may contain high fluoride levels beyond 3 mg/l. In one selected case fluoride levels of about 6 mg/l were identified in groundwater of Madibeng Local Municipality, North West Province of South Africa. West province is one of the areas in South Africa where fluorosis is typical. Areas affected include the North-West provinces, the Karoo, Limpopo and the Northern Cape. Cases like these have attracted research in water defluoridation such that evaluation of activated

alumina as a defluoridating agent was carried out [17 - 19]. The researches demonstrated that the activated alumuna could be employed to treat underground mine water with initial fluoride levels as high as 8 mg/l. Two defluoridation plants were installed each with capacity of 500, 000 litres/day in the early 1980's in the Republic of South Africa.

Location	District	Fluoride level in groundwater (mg/l)	Reference
Bangula market	Nsanje	4.91 ± 0.03	[13]
Nsanje level crossing	Nsanje	7.25 ± 0.01	[16]
Tomali trading centre	Chikwawa	1.91 ± 0.00	[15]
Tomali dip tank	Chikwawa	1.93 ± 0.01	[15]
Mlangalanga Village, Malindi	Mangochi	2.60 ± 0.00	[13]
Mangochi hospital	Mangochi	2.45 ± 0.01	[13]
Nsauya 1	Mangochi	3.64 ± 0.01	[13]
Mbando village	Zomba	6.51 ± 0.01	[13]
Mtubwi	Machinga	7.51 ± 0.00	[14]
Mliwa village	Machinga	5.60 ± 0.00	[13]
Evangelical Baptist Church	Machinga	5.08 ± 0.01	[13]
Machinga hospital	Machinga	4.73 ± 0.01	[14]
Duwa village	Machinga	4.88 ± 0.00	[13]
Chedweka	Machinga	6.47 ± 0.02	[13]
Mazengera	Lilongwe	7.00 ± 0.01	[5]
Nkhotakota boma	Nkhotakota	9.60 ± 0.02	[16]
Songwe	Karonga	8.00 ± 0.01	[16]

Table 6. Some locations with high fluoride levels in groundwater reported in literature

5. Research on fluorosis and water defluoridation

Research on removal of fluoride from drinking water has employed very many materials world over. The main principles however remain adsorption, ion exchange, precipitation, coagulation, membrane processes, distillation and electrolysis.

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5.1. Adsorption and ion exchange

Adsorption involves passage of water through a contact bed where fluoride is removed by ion exchange or surface chemical reaction with the solid bed matrix. After a period of operation, a saturated column must be refilled or regenerated. The different adsorbents used for fluoride removal include activated alumina, carbon, bone charcoal, activated alumina coated silica gel, calcite, activated saw dust, magnesia, serpentine, tricalcium phosphate, activated soil sorbents, carbion, defluoron, and other synthetic ion exchange resins [20 – 24]. Most widely used adsorbents are activated alumina and activated carbon. Activated alumina was first proposed and researched for defluoridation around 1930. It is basically highly porous aluminium oxide with large surface area. The discontinuous cationic lattice of alumina gives it localized areas of positive charge. This renders alumina a good adsorbent for many anionic species, however its greater preference for fluoride compared to other ions has led to its wide use in defluoridation [25]. Defluoridation capacity of activated alumina decreases with increase in hardness. High fluoride concentrations increase the solubility of alumina due to the formation of monomeric aluminium fluoride and aluminium hydroxyl fluoride complexes. It is established that defluoridation with alumina is optimal at pH 5 – 6. The activated alumina does not shrink, swell, soften nor disintegrate when immersed in water but dissolves at pH less than 5.0. At pH greater than 7.0 silicate and hydroxide compete strongly with fluoride for adsorption/exchange sites on alumina resulting in lower fluoride sorption. Chloride does not interfere with sorption of fluoride on activated alumina [23]. The use of activated alumina is highly selective towards fluoride but the pH specificity, low capacity and low material integrity in acidic medium are some of the limitations of this process [20].

It is common to first treat alumina with hydrochloric acid to make it acidic. However this treatment is often carried out in acidic medium with pH between 5 and 6 to avoid excessive dissolution of the alumina that occurs below pH 5. The chloride ions on the acidic alumina are replaced by fluorides when the alumina is in contact with fluoride ions. Equations 3 and 4 below illustrate the activation and ion exchange processes respectively.

$$Al_2O_3{}^{\Phi}H_2O + HCl \rightarrow Al_2O_3{}^{\Phi}HCl + H_2O \tag{3}$$

$$Al_2O_3{}^{\Phi}HCl + NaF \rightarrow Al_2O_3{}^{\Phi}HF + NaCl \tag{4}$$

($Al_2O_3{}^{\Phi}$ indicates activated alumina)

To regenerate the adsorbent a dilute solution of sodium hydroxide is mixed with the adsorbent to get a basic alumina, equation 5, followed by further treatment with acid, equation 6.

$$Al_2O_3{}^{\Phi}HF + 2NaOH \rightarrow Al_2O_3{}^{\Phi}NaOH + NaF + H_2O \quad (5)$$

$$Al_2O_3{}^{\Phi}NaOH + 2HCl \rightarrow Al_2O_3{}^{\Phi}HCl + NaCl + H_2O \quad (6)$$

The regeneration yields sodium fluoride concentrated wastewater that requires disposal, another challenge in the alumina adsorption process. Adsorption with activated carbon is another efficient technique, however, high cost and challenges with the spent carbon limit its large scale application [26]. Granular activated carbon is often employed in adsorption columns because of its non-specific nature of adsorption on its surface [27]. Powdered activated carbon has also been employed successfully in water defluoridation despite that the process is highly pH dependent with optimum results below pH 3 [28]. This requires pH reduction during defluoridation and increasing pH artificially in the water after treatment which is a challenge in the employment of this process. Bone char, which is derived from animal bones charred at 500–600°C, has a rich surface of heterogeneous components, allowing physisorption, chemisorption or ion exchange to occur. Physisorption, also termed physical adsorption, is adsorption that involves van der Waals forces (intermolecular forces) and there are no significant changes in the electronic orbital patterns of the species involved. Chemisorption, on the other hand, involves valence forces of the same kind as those that result in the formation of chemical compounds. The combination of physisorption, chemisorption and ion exchange processes renders bone char a better sorbent, in terms of ion uptake capacity, among other carbon based adsorbents such as activated carbon and peat [29,30]. Bone charcoal has been widely applied in water defluoridation (Castillo et al., 2007 [7, 31,32]. It is typically a black, granular and porous material with about 57 to 80 percent calcium phosphate [$Ca_3(PO_4)_2$], 6 to 10 percent calcium carbonate ($CaCO_3$) and 7 to 10 percent activated carbon. Principal reaction in defluoridation with bone charcoal is hydroxyl-fluoride exchange of apatite, equation 7 [3].

$$Ca_{10}(PO_4)_6(OH)_2 + 2F^- \rightarrow Ca_{10}(PO_4)_6F_2 + 2OH^- \quad (7)$$

The preparation of bone charcoal is crucial. Unless carried out properly, the bone charring process may result in a product of low defluoridation capacity and/or deterioration in aesthetic water quality. Water treated with poor bone charcoal may taste and smell like rotten meat and is aesthetically unacceptable [3,7].

5.2. Precipitation – Coagulation

The Nalgonda technique is a widely known precipitation – coagulation defluoridation method. In this technique aluminium sulfate and lime are added periodically in batch to treat water. These are co-precipitation chemicals that behave as shown, equations 8 - 11, in fluoride removal.

$$Al_2(SO_4)_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3SO_4^{2-} + 6H^+ \quad (8)$$

$$Al(OH)_3 + F^- \rightarrow Al - F_{Complex} + undefined_{\ ppt} \quad (9)$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (10)$$

$$3Ca(OH)_2 + 6H^+ \rightarrow 3Ca^{2+} + 6H_2O \quad (11)$$

Other co-precipitation chemicals such as polyaluminium chloride (PAC), lime and similar compounds are also employed and are added daily to raw water in batches. Precipitation techniques produce a certain amount of sludge every day [3].

Calcium and phosphate compounds are an example of contact precipitation chemicals often added to the water upstream of a catalytic filter bed. In contact precipitation there is no sludge and no saturation of the bed, only the accumulation of the precipitate in the bed. Theoretically it is possible to precipitate fluoride as calcium fluoride or fluoroapatite in solutions containing calcium, phosphate and fluoride; however in practice it is kinetically impossible. The reaction kinetics are very slow. Precipitation is easily catalysed in a contact bed that acts as a filter for the precipitate. The reactions involve dissolution of calcium chloride and sodium dihydrogen phosphate, and consequent precipitation of calcium fluoride and fluoroapatite [33]. These are illustrated through equations 12 to 15.

$$CaCl_{2(aq)} \rightarrow Ca^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)} \quad (12)$$

$$NaH_2PO_{4(aq)} \rightarrow Na^+{}_{(aq)} + 2H^+{}_{(aq)} + PO_4^{2-}{}_{(aq)} \quad (13)$$

$$Ca^{2+}{}_{(aq)} + 2F^-{}_{(aq)} \rightarrow CaF_{2(s)} \quad (14)$$

$$10Ca^{2+}{}_{(aq)} + 6PO_4^{2-}{}_{(aq)} + F^-{}_{(aq)} \rightarrow Ca_{10}(PO_4)F_{2(s)} \quad (15)$$

A small saturated bone char contact bed is employed as a column. This column is supported by coarse grain charcoal or gravel. Figure 8 shows the Ngurdoto configuration [34].

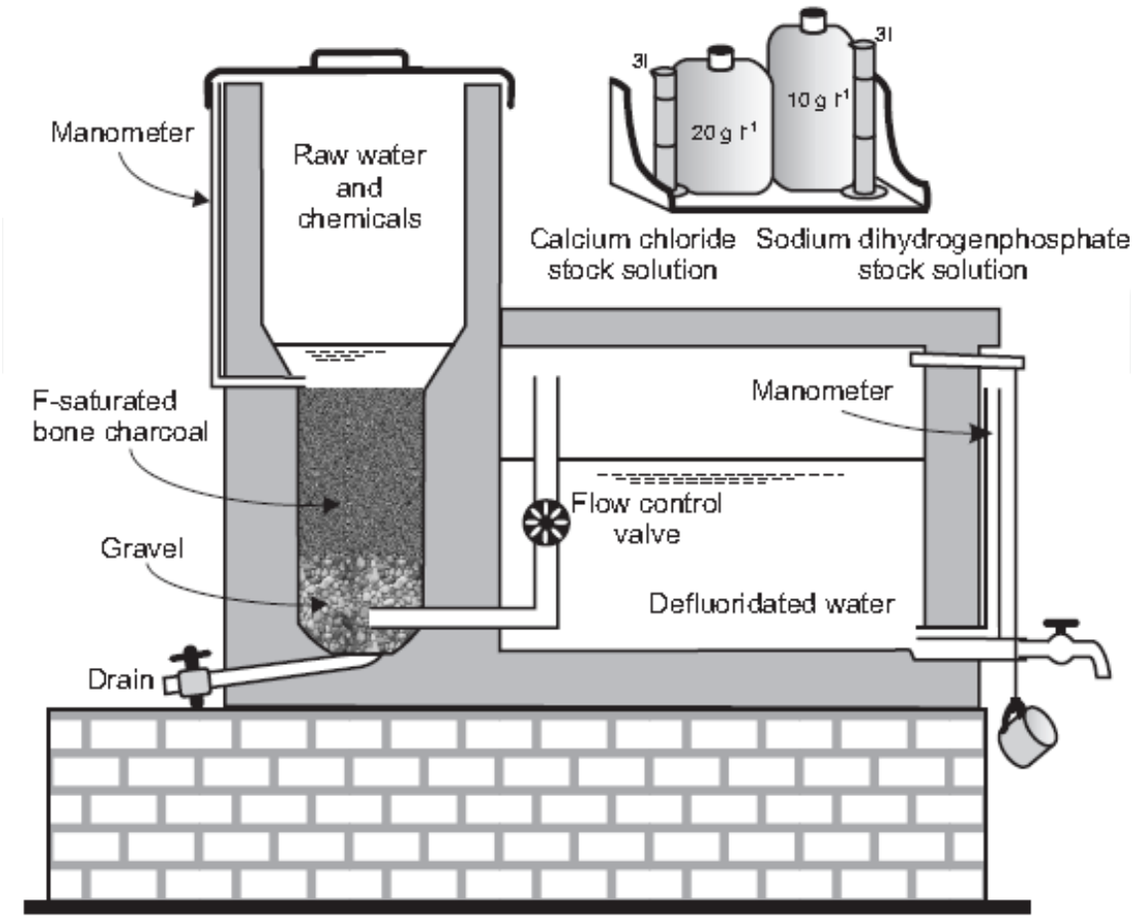


Figure 8. Contact precipitation of fluoride as invented in Ngurdoto

It is recommended to prepare the chemicals monthly as stock solutions and employ them in aliquots. The two stock solutions should not be mixed before treatment in order to avoid the precipitation of calcium phosphate. Two special measuring cups may be used for volumetric portioning of the chemicals. It is advisable to check the bulk density as it may vary for different brands. The stock solutions, stored in Jerry cans, along with the respective chemical bags and the measuring cups and cylinders may be coloured red and green respectively in order to minimize the risk of exchange and so incorrect dosage [3]. The design criteria of the contact precipitation plants is simple however, the theoretical background is fairly complex and largely dependent on the reactions shown in equations 14 and 15. The extent to which each reaction occurs is not well understood. In calcium fluoride precipitation, the Ca/F weight ratio is about 1, equivalent to a CC/F ratio of about 4. In fluorapatite precipitation, the Ca/F ration is 11 and the PO_4/F ratio is 15, equivalent to a CC/F ratio of about 39 and a MSP/F ratio of about 23. This implies that the more fluoride precipitated as calcium fluoride, rather than as fluorapatite, the lower is the required dosage of chemicals. Calcium fluoride precipitation is probably more dominant with higher raw water fluoride concentration. Experience from operations of the contact precipitation in Tanzania, where the fluoride concentration averages 10 mg/l, has shown that the process functions effectively when the dosage ratios are 30 and 15 for CC and

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MSP respectively. This dosage would ensure at least 65 per cent precipitation of fluorapatite and a surplus of calcium for precipitation of the residual fluoride as calcium fluoride [33,34].

5.3. Membrane filtration

Membrane filtration processes are among advanced water treatment technologies that have been mainly employed in treatment of pure and ultra pure water. The US EPA, 2003, recommended reverse osmosis, RO, as one of the best available defluoridation technologies [35]. Reverse osmosis and nano-filtration (NF) are the well known membrane technologies that can remove a large spectrum of contaminants from water such as pathogens, turbidity, heavy metals, salinity, natural and synthetic organics, and hardness [36]. The two processes are highly effective in water defluoridation and produce high quality water that includes disinfection during water treatment. NF membranes operate at a lower pressure and have lower capacity as compared to RO membranes. Another membrane technology is electrodialysis. Use of electrodialysis plants in North Africa is employed in large scale water treatment of high fluoride brackish water for potable water supply [37]. Electrodialysis is similar to Reverse Osmosis, except it uses an applied direct current potential instead of pressure, to separate ionic contaminants from water. Water does not physically pass through the membrane in the electrodialysis process as such particulate matter is not removed. The ED membranes are therefore not technically considered filters. The water quality from electrodialysis treatment is comparable to RO, and may require post-treatment stabilization. The process tends to be most economical for source water with TDS levels in excess of 4,000 mg/L. It is established that RO and electrodialysis have very high defluoridation capacities (85 – 95 %) and function effectively in any pH range. However the water loss is high (20 - 30 % for electrodialysis, 40 – 60 % for RO), have high capital cost and are energy intensive [37]. Membrane technologies often require special equipment, electrical energy and specialized training for operators as such the capital and operation costs are high. Low applicability is therefore envisaged for rural sectors of the developing countries where energy and trained human resource are often deficient.

5.4. Emerging technologies

Some emerging technologies employing precipitation, distillation and /or a combination of principles are; The Crystalactor®, Memstill® technology, The WaterPyramid® solution and The Solar Dew Collector system. The Crystalactor® was developed by DHV in the Netherlands [38]. It is a pellet reactor employing a fluidized bed. Water defluoridation occurs in the reactor accompanied by formation of calcium fluoride pellets of 1 mm diameter. The Crystalactor® employs contact precipitation and has the strengths that; the installation is compact, produces usable calcium fluoride pellets with high-purity, and the produced pellets have extremely low water content (5% to 10% moisture). It is estimated that this technology costs about a quarter of the conventional precipitation techniques. The technology is however suitable for treating high fluoride waters (>10 mg/l) and to attain concentrations below 1 mg/l a second treatment is often required. A membrane based distillation concept is also reported as developed by the Netherlands Organisation of Applied Scientific Research (TNO), the Memstill® technology,

Figure 11. This technology advances ecology and economy of the existing technologies in brackish and sea water desalination. The technology also removes other anions such as fluoride and arsenic [39]. In the Memstill® technology cold feed water takes up heat in the condenser channel through condensation of water vapour, then a small amount of (waste) heat is added, and flows counter currently back via the membrane channel. This small added heat evaporates water through the membrane. The water is discharged as cold condensate. The cooled brine is disposed, or extra concentrated in a next module. The Memstill® technology can produce potable water at a cost well below that of existing technologies like reverse osmosis and distillation. It is expected that the Memstill® technology will also be developed for small scale applications using solar heat [39].

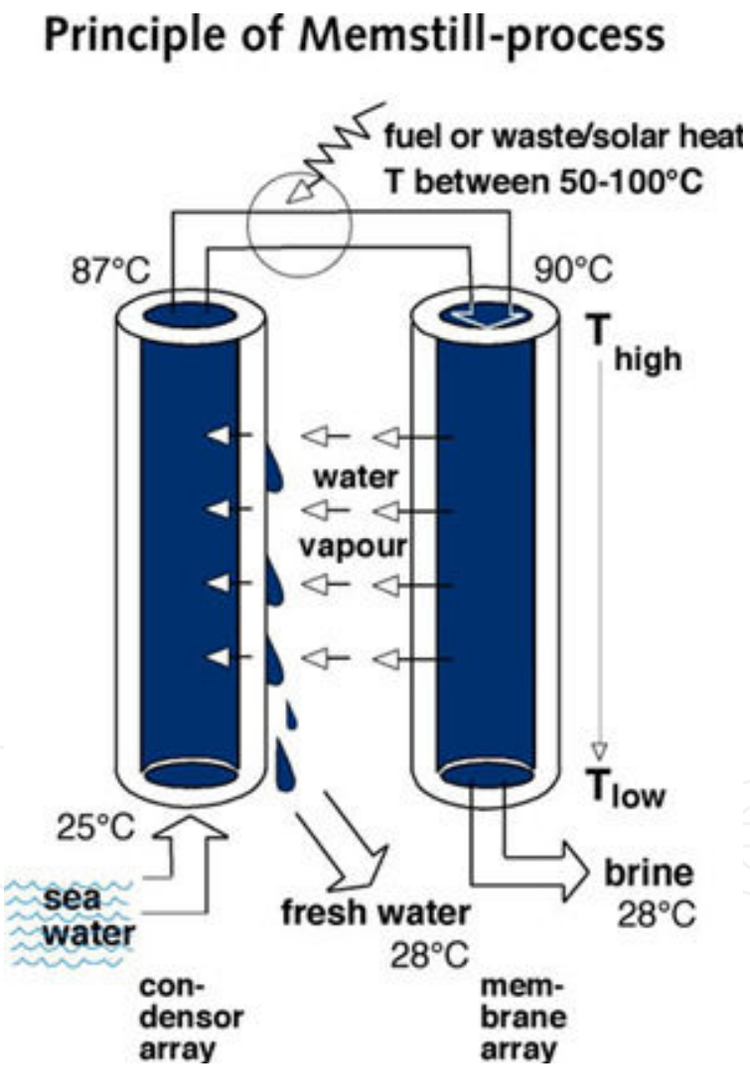


Figure 9. Memstill® technology [39]

The water pyramid, developed for rural tropical areas, employs solar energy to produce potable water from saline, brackish or polluted water, Figure 12 [40]. The technology also removes fluoride. A water pyramid with a total area of 600 m^2, placed under favourable tropical

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conditions, can produce about 1250 litres of fresh water a day. The rate of production is however dependent on local atmospheric conditions such as climate, temperature, cloud-cover and wind activity. Solar energy drives the desalination while energy required for pressuring the WaterPyramid® is obtained using solar cells combined with a battery backup system. A small generator may be required to cater for intermittent peak demands in electricity.



Figure 10. The WaterPyramid® [40]

Another technique similar to the WaterPyramid was developed by Solar Dew, Figure 13 [41]. This is a porous membrane that purifies water using solar energy. In this techniques water sweats through a membrane and evaporates on the membrane surface. This increases humidity in the evaporation chamber. As a result of temperature difference pure water condenses on the cooler surface of the system.

Larsen and Pearce, 2002, proposed a defluoridation method in which fluoride containing water is boiled with brushite ($CaHPO_4.2H_2O$) and calcite ($CaCO_3$). Good results were obtained on laboratory scale. Larsen and Pearce concluded that boiling brushite and calcite in fluoritic water yields fluoroapatite which results in defluoridation [42].

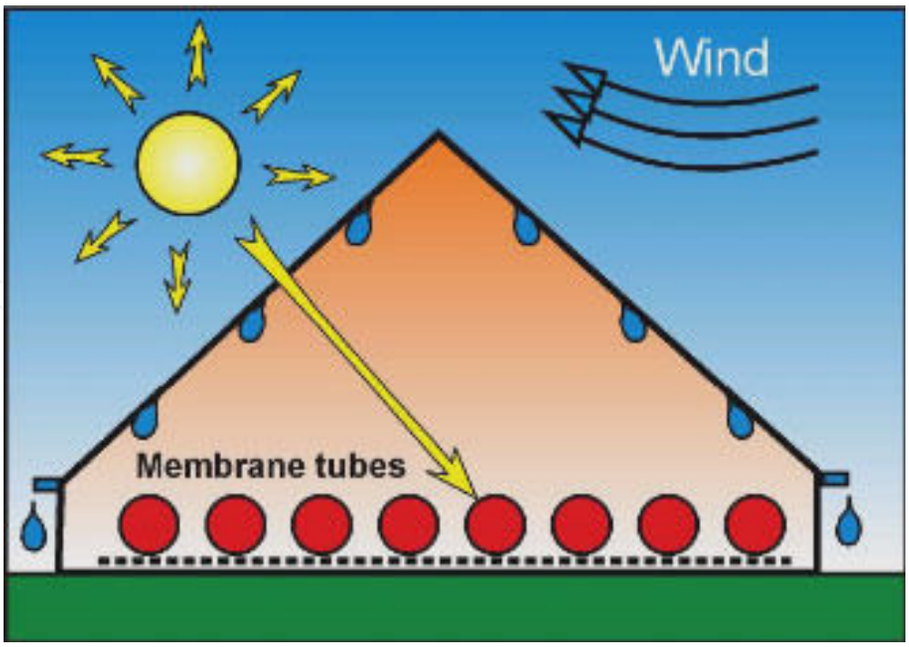


Figure 11. The Solar Dew Collector system [41]

6. Research on fluorosis and water defluoridation in East and Southern Africa

Research was carried out in Tanzania at Ngurdoto Defluoridation Research Station employing different materials in batch and fixed bed defluoridation configurations. In Malawi Research was carried out at Chancellor College of the University of Malawi. Bone char, bauxite, gypsum, magnesite have been experimented on in defluoridation.

6.1. Water defluoridation research in Tanzania

Removal of fluoride from water has been researched on employing a number of materials among which are bauxite, gypsum, magnesite and their composite filters [2,46,47], Calcium chloride ($CaCl_2$) and Sodium dihydrogen phosphate (NaH_2PO_4) as co-precipitation reagents in contact precipitation [33, 34], cow bone char in batch and fixed bed [7, 32], fish bone [43], activated carbon and activated carbon loaded separately with alumina, magnesia and calcium [44], and, magnesite [45].

Research on defluoridation with bauxite, gypsum and magnesite focused on developing a hybrid technology with the three materials to reduce negative impacts on water quality that are encountered when each of the materials i.e. bauxite, gypsum and magnesite, is employed alone. The composites tested were mixtures of bauxite, gypsum and magnesite in respective mass ratios of 1:2:3, and such combinations with the order of the ratio numbers varied, giving a total of six compositions. Different calcine temperatures ranging from 150 to 500 ^{o}C were also tested and performance of batch and fixed bed configurations were compared. The research results in summary showed that the fixed bed configuration of the 3:2:1 (mass ratio of bauxite,

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gypsum, magnesite respectively) obtained water of optimum quality when calcined at 200 °C. The water quality parameters included in this research were pH, alkalinity, apparent colour, concentrations of the ions F^-, Cl^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Fe^{2+}, Al^{3+}, and hardness. The World Health Organisation recommended limits were employed as bench marks [48]. Table 7 illustrates the problems that were addressed by this research and potential solutions obtained.

Material	Challenge	Result Obtained	Proposed Solution
Bauxite	High turbidity, above 1 NTU, in treated water when used raw	When calcined above 200 °C and employed in fixed bed turbidity reduced to below 1 NTU	May use bauxite calcined at 200 °C in fixed bed to reduce turbidity
	Residual colour beyond 50 TCU	The composite 3:2:1 of bauxite, gypsum and magnesite calcined at 200 °C obtained colours below 50 TCU in fixed bed.	Combine the materials in this ratio and calcine at 200 °C, employ in fixed bed
	Residual Al^{3+} beyond 0.2 mg/l	The composite 3:2:1 of bauxite, gypsum and magnesite calcined at 200 °C obtained Al^{3+} concentrations below 0.2 mg/l in fixed bed.	As above.
Gypsum	Residual hardness above 500 mg/l as $CaCO_3$	The composite 3:2:1 of bauxite, gypsum and magnesite calcined at 200 °C obtained hardness below 500 mg/l as $CaCO_3$ in fixed bed.	As above.
	High residual SO_4^{2-} beyond 400 mg/l	Gypsum calcined at 400 °C obtained residual sulphates lower than 100 mg/l, composite 3:2:1 calcined at 200 °C employed in fixed bed obtained similar results & higher loading capacity.	May employ calcined gypsum but composite has higher loading capacity therefore composite is better choice to gypsum
Magnesite	Residual pH above 8.5	Composite described above obtained pH between 6.7 and 8.0 in fixed bed	Composite may be used instead of magnesite.

Table 7. Major findings in defluoridation with bauxite, gypsum and magnesite at Ngurdoto

Bauxite obtained from Kwemashai in Lushotho District of Tanzania when characterised for composition showed that the major components were Al_2O_3 (30.33%), SiO_2 (15.00%) and Fe_2O_3 (14.30%). Fluoride removal with bauxite is known to depend mainly on reactions of the Al_2O_3 . Oxides of aluminium are amphoteric and will react as base or acid represented in Equations 16 and 17 respectively.

$$Al_2O_3(s) + 6H_3O^+(aq) + 3H_2O(l) \rightarrow 2[Al(OH_2)_6]^{3+}(aq) \quad (16)$$

$$Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2[Al(OH)_4]^-(aq) \quad (17)$$

Defluoridation capacity of bauxite decreased with increase in pH of the medium, a result attributed to dominance of acidic reaction of Al_2O_3 shown in Equation 17 with formation of negatively charged species. The negatively charged species would in effect retard fluoride sorption. Formation of positively charged species as shown in Equation 16 would occur in low pH medium hence greater adsorption of fluoride, fluoride being an anion [46,47].

Contact precipitation of fluoride was also researched on at Ngurdoto [33,34]. The technique employed Calcium chloride and Sodium dihydrogen phosphate and has been described in section 2.4.2. The technology best demonstrated in Tanzania is use of bone char at household level in fixed bed. The configuration designed at Ngurdoto Research Station is shown in Figure 12.



Figure 12. Household defluoridation unit employing bone char developed by Ngurdoto Research Station shown in average and low income household settings

This column for fixed bed defluoridation has also been scaled up particularly in Arusha national park by the Ngurdoto defluoridation station shown in Figure 13.

Clean raw cow bones are collected and charred at 500 – 550 ^{o} C in specially designed kilns in which air supply is controlled, Figure 14. The charred bones are pulverized to particle sizes of range 0.5 to 3 mm in diameter.

The bone char has high sorption capacity initially however the media gets saturated with fluoride with time. The general practice around Arusha is to replace the media when the effluent has a fluoride concentration of 2 mg/L, the maximum permissible limit as per International Reference Centre (IRC) in the Hague, Netherland. Results obtained from a typical bone char household unit are shown in Figure 17. The figure shows that defluoridation of water with initial fluoride of 10 mg/L up to about 1300 litres of treated water are obtained with fluoride less than 2 mg/L. The mass of bone char used in this investigation was 4 kg. Based on use of 20 litres per family per day of the treated water, the 4 Kg of bone char can be employed

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Figure 13. Incomplete and completed community defluoridation unit designed by Ngurdoto Defluoridation research station



Figure 14. Different sizes of bone charring kilns as developed at the Ngurdoto Defluoridation Research Station

to treat water for sixty five days family use. This approximates to 20 to 25 kg of bone char in a year for a family.

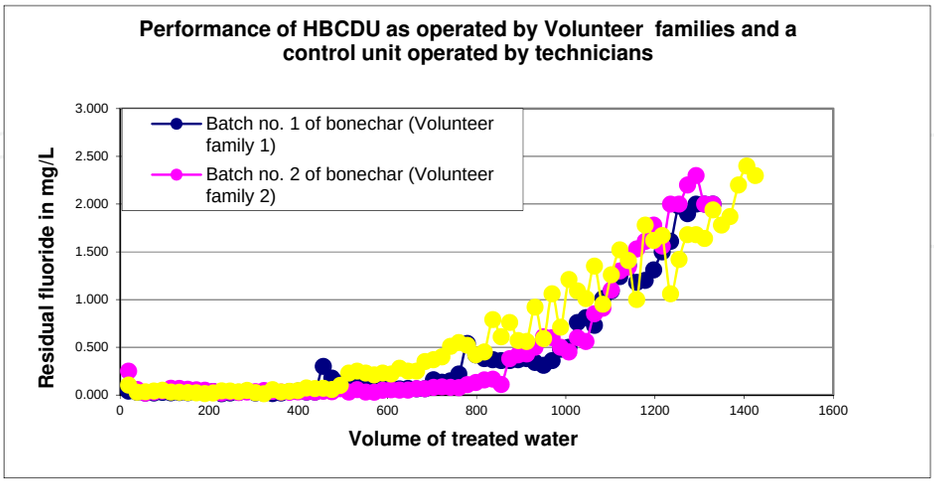


Figure 15. Plot of residual fluoride against volume of treated water for household column units (obtained from Ngurdoto research station development report, 2010)

Investigations have shown that the higher the initial fluoride concentration the higher the bone char exhaustion rate and the smaller amount of bone char the faster the exhausted rate. Fixed bed defluoridation had better performance compared to defluoridation in batch.

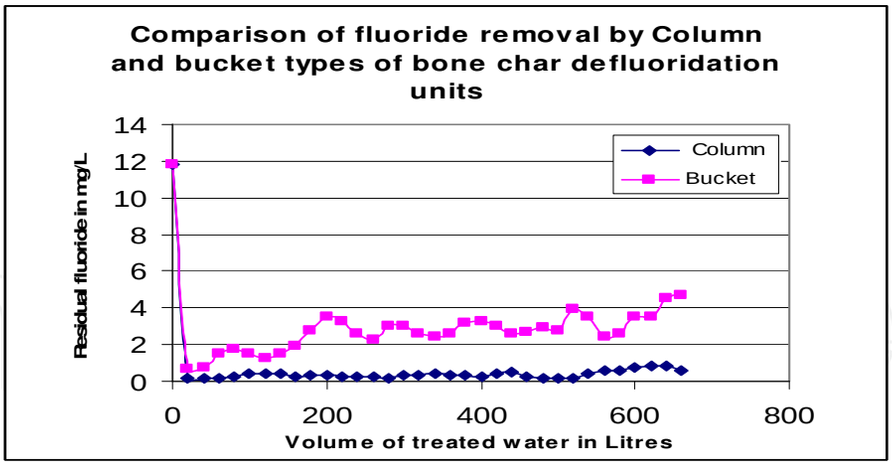


Figure 16. Residual fluoride obtained in column and bucket defluoridation.

6.2. Water defluoridation research in Malawi

Water defluoridation research in Malawi has been tested with bauxite, gypsum, clay, synthetic and natural hydroxyapatite (HAP) [5, 13, 14]. Gypsum was obtained from Mponela, in Dowa Diastrict of Malawi. Bauxite was obtained from Mulanje Mountain in Mulanje, Malawi and

natural hydroxyapatite was obtained from Phalombe District, Malawi. Clay was obtained from Namadzi, Chiradzulu District of Malawi. The materials were calcined at various temperatures, within range 200 to 600 °C, for two hours. Bauxite obtained highest sorption capacity (3.05 mg/g) when calcined at 200 °C. Gypsum obtained highest capacity, 2.17 mg/g, when calcined at 400 °C. Clay obtained highest capacity, 2.15 mg/g, when calcined at 300 °C. Synthetic hydroxyapatite had a fluoride sorption of 1.70 mg/g. Preparation of synthetic hydroxyapatite involved controlled addition of 98 % H_3PO_4 in an aqueous suspension of CaO with periodic additions of 50 % aqueous ammonia. This was followed with decanting the supernatant and then drying the remaining precipitate at 60 °C overnight. The product was then sintered at 1100 °C [49]. The synthetic hydroxyapatite was thus not calcined to various temperatures because its preparation involved high temperature. The natural hydroxyapatite introduced more fluoride in the water with residual fluoride increasing from 8.0 mg/l to 9.65 mg/l. X-Ray Diffraction (XRD) characterisation showed the material composition were as shown in Table 8.

Raw material	Major compound composition as per JCPDS [50]
Bauxite	$Al_2Si_2O_5(OH)_4$
Gypsum	$CaSO_4.2H_2O$
Clay	
Synthetic HAP	$Ca_5(PO_4)_3OH$
Natural HAP	$Ca_5(PO_4)_2CO_3(OH)F$, $Ca_5Al_2(OH)_4Si_3O_{12}$, $Ca_5(PO_4)_3F$

Table 8. Major compounds in bauxite, gypsum, clay, synthetic and natural HAP tried in Malawi

The natural HAP contained fluoride that explained why it acted as a fluoridating agent. The research also showed that initial quality of the raw water impacts on the defluoridation capacity of the materials tested. Higher initial concentrations of carbonates and chlorides reduced fluoride sorption whereas high initial concentrations of calcium enhanced the sorption in defluoridation with bauxite. In defluoridation with gypsum the higher the initial concentrations of carbonate, nitrate and chloride ions the lower was the sorption of fluoride. Phosphate and chloride interfered with fluoride sorption in defluoridation with synthetic hydroxyapatite.

7. Overview of defluoridation technologies

Table 9 illustrates typical defluoridation outcomes and limitations when different materials are employed. The principals involved in the technologies are briefly outlined in the table to summarise the defluoridation techniques that have been widely demonstrated.

Technology/ Material	Typical capacities (mg/g)	The science	Strengths	Limitations
Activated alumina	3.5– 10.0	Precipitations involving $Al_2O_3$and in F^-ions water	High selectivity for fluoride	lowers pH of water, residual Al^{3+}
Nalgonda	0.7 – 3.7	Reactions of Alum, $Al_2(SO_4)_3$and lime (CaO)	Same chemicals used for ordinary water treatment	High chemical dose, high sludge disposal required
Bone char	2.3 – 4.7	Filtration and ion exchange in $Ca_5(PO4)_3OH$ structure	Availability of raw materials	Not universally acceptable
Bauxite	3.0 – 8.9	Precipitations involving Al_2O_3andF^- and other oxides e.g. Fe_2O_3ions water	Available locally in some areas. High capacity	Residual colour and turbidity in treated water if used raw
Gypsum	1.1 – 6.8	Ion exchange involving $CaSO_4$and F^- and other compounds e.g. $Ca(OH)_2$	Locally available in some areas	High Residual Calcium sulphate
Magnesite	1.0 – 3.7	Ion exchange and precipitation involving MgOandF^- and other compounds e.g. $Mg(OH)_2$	Simple technique, locally available in some areas	High pH & residual Mg.
HAP	0.5 – 2.9	Ion exchange and precipitation involving $Ca_5(PO_4)_3OH$ andF^- and other compounds e.g. $Ca_5H(PO_4)_3(OH)_2$	Naturally available in some areas	Residual Phosphate
Bauxite, gypsum, magnesite composite	4.2– 11.3	ion exchange and precipitation in reactions of $Al_2O_3,\ CaSO_4,\ MgCO_3,\ MgO$	Simple and versatile. Better than use of each of the materials	Energy intensive, fairly novel technique.
Zeolites	28 - 41	ion exchange and surface complexation reactions	High capacity	Limited availability
Other advanced techniques	High	Nano-filtration, Reverse osmosis, distillation, precipitation, electrolysis	Very high capacities	High cost. Need for special training

Table 9.

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8. Chapter conclusion

There is a wide range of defluoridation techniques and materials to employ when fluoride levels in potable water are likely to result in fluorosis. However the decision on limits of fluoride concentrations in potable water for any region must be guided by average annual daily temperatures, dietary habits, nature and levels of activities in the particular area. Choice of technology will depend on appropriateness where factors such as availability of materials, cost, level of defluoridation required and technical complexity need to be considered. In East and Southern Africa naturally occurring materials such as bone, limestone ($CaCO_3$), alum (Al_2SO_4), bauxite, gypsum, magnesite, and such other available materials with fluoride affinity, may be given priority when selecting raw materials for treatment and use in water defluoridation. Adoption and/or adaptation of existing technologies require some research at local level because communities differ in socio, economic, religious and traditional status and norms. A basic level of research is therefore paramount to establish appropriateness of a preselected technology to ascertain sustainability of the intervention.

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