

*Full Length Research Paper*

# Groundwater fluoride levels in villages of Southern Malawi and removal studies using bauxite

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Dental and skeletal fluorosis are known to be caused by excessive fluoride ingestion particularly from drinking water sources. Dental fluorosis is common in some parts of Malawi but studies on fluoride levels of drinking water sources have not been adequately done. This paper presents our findings in fluoride levels of some drinking water sources in selected rural areas of Southern Malawi and studies on the potential of locally sourced bauxite in water defluoridation at laboratory scale. The work has revealed high levels of fluorides (>1.5 mg/L) in some parts of the study area. A positive correlation was observed between the pH of the water and fluoride concentrations. No correlation existed between fluoride concentration and electroconductivity. Experiments on water defluoridation with bauxite showed that the raw bauxite has a capacity of 93.8 % at a dose of 2.5g/200 ml of 8 mg/L F<sup>-</sup> solution. Powder X-ray diffraction characterization of the raw bauxite showed gibbsite (Al(OH)<sub>3</sub>) and kaolinite (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>) as the major components. The high defluoridation capacity of the bauxite is thus attributable to gibbsite and kaolinite minerals. Precipitation of AlF<sub>3</sub> is predicted to be the fluoride removal mechanism with the gibbsite while exchange of OH<sup>-</sup> groups in the gibbsite layers of the kaolinite with F<sup>-</sup> ions occurs in the kaolinite component of the defluoridation material. Evaluated by the residual fluoride concentration in solution the fluoride uptake reaction kinetics of the system was found to be consistent with pseudo-first-order kinetics.

**Key words:** Fluoride, bauxite, Southern Malawi, gibbsite, kaolinite.

## INTRODUCTION

Groundwater contributes only 0.6% of the total water resources of the earth (Meenakshi and Mehshwari, 2006); however, it is the major and most preferred source of drinking water in rural as well as urban areas in developing countries because it does not require treatment. Efforts in addressing water issues in Malawi concentrate on bringing water to the people with little attention to water quality (NEP, 1996; SEP, 1998). In 1993, 24% of rural population depended on boreholes for domestic water supply, 22% relied on tap water, 6% on shallow wells and 48% had no access to safe water (GoM, 1993). Various natural and anthropogenic ecological factors pollute the groundwater because of deep percolation from

intensively cultivated fields, disposal of hazardous wastes, liquid and solid wastes from industries, sewage disposal and surface impoundments (Anwar, 2003; Oren et al., 2004; Amina et al., 2004; Kass et al., 2005). Fluorides are one such type of contaminants that leach from rocks and soils into ground water. The high fluoride ground waters are generally of the sodium-chloride, sodium-calcium-chloride or sodium-bicarbonate-chloride types characterized by a moderately high pH value in the range 8.2 to 9.4 pH units (Kohut and Hodge, 1985).

Fluoride is toxic at concentrations greater than 1.5 mg/L and is associated with dental fluorosis (Harper et al, 1979). At fluoride levels between 3.0 to 6.0 mg/L in drinking water skeletal fluorosis may be observed and when a concentration of 10 mg/L is exceeded crippling fluorosis can ensue. Recent investigations have shown that non-skeletal fluorosis whereby soft tissues are affected can

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also occur due to prolonged intake of fluoride in high concentrations (Mjengera and Mkongo, 2003). In Malawi, cases of dental fluorosis are very common in localized parts of the country. At Mtubwi Primary School in Machinga District, for example, mild to severe dental fluorosis cases in Standard 3 and 4 pupils has been determined to be 50 to 80% (Sajidu et al., 2005).

Some of the solutions to fluoride and fluorosis problems are; change to alternative sources of drinking water, improvement in nutritional status of the people at risk and defluoridation which is the removal of excess fluoride in the water. In most rural areas where alternative sources of water are unavailable, defluoridation may offer a practical solution to the problem. Several methods of excess-fluoride removal from portable water are used in many countries.

The Nalgonda technology where aluminium sulphate is added to precipitate fluorides in raw water to which lime may be added to obtain the appropriate alkalinity (Susheela, 1992) is one such defluoridation technique. The major concerns with this technique are that the doses of alum and lime are determined after assessing the fluoride levels and alkalinity of the water changes with season, and, if the alum dose is not adhered to there is a possibility of excess aluminium contamination in the water (Susheela, 1992).

Clays and soils have been studied for water defluoridation after the work of Bower and Hatcher (1967). Their work showed positive results in fluoride removal particularly in the case of aluminium hydroxide (gibbsite). Following this study, many soils and clay minerals have been investigated. Illinois soils in the USA (Omueti and Jones, 1977), sodic soils in India (Chhabra et al., 1980), activated alumina (Schoeman and MacLeod, 1987), electro-activated alumina (Lounici et al., 2004), combination of aluminium and zirconium oxide with specific Donnan dialysis (Garmes et al., 2002), electrocoagulation and floatation processes using monopolar aluminium electrodes (Emamjomeh and Muttucumar, 2006), clay pottery (Chaturvedi et al., 1988), Ando soils in Kenya (Zevenbergen et al., 1996), fired clay chips in Ethiopia (Moges et al., 1996), fly ash (Chaturvedi et al., 1990), kaolinite (Kau et al., 1997), illite-goethite soils in China (Wang and Reardon, 2001), South African clays and bauxite (Coetzee et al., 2003; Das et al., 2005) have been studied.

Charred bone at 550°C has also been employed in the bone charcoal defluoridation technology (PHE 2001). The bone charring process if not properly carried out results in a product of low defluoridation capacity that leaves the treated water with a rotten meat taste and smell. The whole process from bone preparation to charring and application may take over 24 h. Other carbonaceous materials in addition to the bone char have also been investigated for defluoridation (Abe et al., 2004). Methods based on use of anion exchange resins under electrodialysis conditions (Zen et al., 2005; Tor, 2006) and nanofil-

tration membranes (Hu and Dickson, 2006) have also been reported.

In Malawi, free fluoride levels of up to 8.6 mg/L in borehole water have been reported at Ulongwe in Machinga District (Sibale et al., 1998), 7 mg/L at Mazengera and Nathenje in Lilongwe, 9.6 mg/L in Nkhotakota, 8.0 mg/L in Karonga, 5.8 mg/L in Nsanje and 3.4 mg/L in Mwanza (Carter and Bennet, 1973; Msonda, 2003). This calls for water defluoridation technologies in Malawi since the levels are way above the WHO guideline value of 1.5 mg/L. Earlier studies had shown that clays can effectively be used for water defluoridation in the country (Msonda, 2003). Our group has shown high defluoridation capacity of locally sourced gypsum (Masamba et al., 2005). A dose of 10 g gypsum calcined at 400°C in 200 ml of 8 mg/L fluoride solution resulted in about 70% fluoride removal within equilibration time of 30 min.

This work was therefore aimed at providing more data on water fluoride levels in the country (particularly in the Southern region). The work also investigated the potential of bauxite in water defluoridation at laboratory scale.

## MATERIALS AND METHODS

### Chemicals and reagents

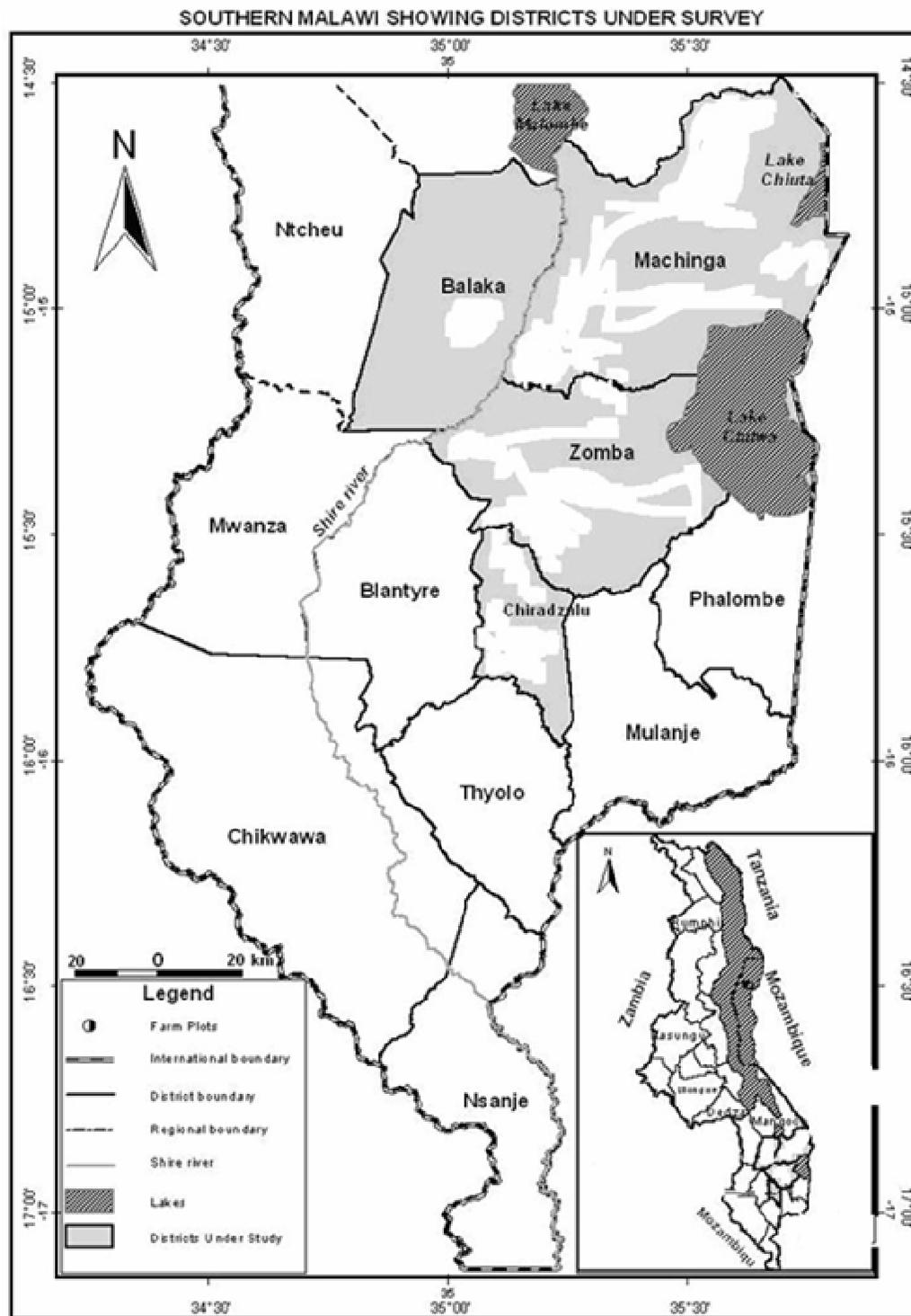
Analytical reagent grade chemicals for analyses were purchased from Technilab Company (Ltd), Blantyre, Malawi. Deionised water was used in all solution preparations and analyses.

### Water fluoride levels in selected rural areas of Southern Malawi

The Southern Region of Malawi consists of 12 districts of the total 27 districts in the country (Figure 1). It covers an area of 31,753 km<sup>2</sup> and it is the most densely populated region with a population of 5,345,045. Due to lack of data on fluorosis cases in health authority offices, selection of sampling sites was based on dental technicians' perception of areas thought to be fluorosis endemic. The sites included six boreholes in Nsanje district, four boreholes and one river in Chikwawa district, eleven boreholes in Zomba, eleven boreholes in Machinga district and sixteen boreholes in Mangochi district. Samples were collected in triplicate at each sampling point into thoroughly rinsed one-litre polythene bottles. Concentration of fluoride was determined using a fluoride ion specific electrode (Orion number 9409) with Sargent Welch pH/activity meter model PAX 900. The sample or the standard solution (25 ml) was initially mixed with 25 ml of total ionic strength adjusting buffer (TISAB) which had been prepared according to recommended procedure in order to provide stable analytical conditions by adjusting pH and complexing interfering ions. The samples were also tested for pH (on site at each water source) and electrical conductivity (EC).

### Use of bauxite for water defluoridation

Raw bauxite for defluoridation work was obtained from the Geological Survey of Malawi in Zomba but was originally acquired from Mulanje mountain in Mulanje district. The bauxite was ground into powder form. It was then calcined in air using a muffle furnace at temperatures of 200, 300, 400, and 500°C to acquire different phases of bauxite for experimentation so as to determine the phase



**Figure 1.** Map of Southern Region of Malawi showing all districts including those under study.

with the highest defluoridation capacity. The samples were held at each reaction temperature for 2 h and quench-cooled to room temperature. Defluoridation capacity determinations were carried out by mixing 200 ml of 8 mg/L fluoride solution with 2.5 g of defluoridating material (bauxite or a calcined phase of bauxite) and shaking for 30 min. Fluoride concentration in the solution was monitored hourly for

12 h. Fluoride levels in water samples were determined as described in section 2.2 above. To determine the effect of bauxite on water quality pH, aluminium, silicon, sulphate, carbonate and phosphate concentrations in water were determined. Aluminium and silicon were analysed using Atomic Absorption spectrophotometry. Sulphates were determined by a turbidimetric method on Jenway

6405 UV-Visible spectrophotometer, phosphates were determined through a vanadomolybdophosphoric acid colorimetric method and carbonates were determined titrimetrically as described in APHA (1985). The percent defluoridation capacity (%E) was calculated as follows:

$$\% E = \frac{(C_o - C) \times 100}{C_o}$$

where  $C_o$  and  $C$  are the initial and final (after defluoridation) concentrations respectively of the fluorides in solution. The raw bauxite was characterized by powder X-ray diffraction (PXRD) using Shimadzu 600 X-Ray Diffractometer. The PXRD patterns were collected in continuous scan mode with monochromatic  $\text{CuK}\alpha$  ( $\lambda=1.5418 \text{ \AA}$ ) radiation that was selected using a curved germanium (111) monochromator. X-rays which were produced at the X-ray source (copper radiation) were reflected at the germanium monochromator (111 planes) giving pure  $\text{CuK}\alpha$  radiation which was diffracted by the sample. The data were collected in the range from  $10.0$  to  $80.0^\circ$  ( $2\theta$ ) by a linear PSD which was set at a step size of  $0.5^\circ$  ( $2\theta$ ) and counting time of 60s per step. Compound identification was made using a search-match computer program supported by the Joint Committee on Powder Diffraction Standards database JCPDS (1997) together with diffraction profiles obtained from standards of bauxite and clay minerals as reported in literature (Mineral database, 2002). In order to determine the dehydration temperature and also the amount of water in the bauxite occurring both as surface physisorbed water and water coordinated to the bauxite, thermogravimetric analysis (TGA) was approximated by heating the bauxite sample in air in a muffle furnace at increasing specified temperatures and measuring the weight loss of the material using an analytical balance.

## RESULTS AND DISCUSSION

### Water fluoride levels in selected rural areas of Southern Malawi

Tables 1a and b give the groundwater fluoride levels in the sampled areas of Southern Malawi. The fluoride data at twenty-one of the forty-nine sampled locations was found to be above the WHO maximum limit of 1.50 mg/L. Five out of the six (83%) sampled boreholes in Nsanje showed fluoride levels above 1.5 mg/L ranging from 1.65 to 7.50 mg/L. Nsanje is one of the districts in the country where sight of dental fluorosis amongst the locals is common. This could therefore be attributable to high levels of fluorides in the ground water. The other notable district is Machinga particularly in Liwonde neighbourhood which encompasses the eleven sampled boreholes in the district. Of the eleven sites studied in the Liwonde neighbourhood, eight (73%) indicated high levels of fluoride, higher than 2 mg/L in all cases. The results extend the database of fluoride levels in this area since the earlier study by Sibale et al. (1998) only looked at one borehole (Mtubwi B/H). Only one borehole in Zomba district at Mbando village which is close to Lake Chilwa indicated high fluoride levels ( $6.51 \pm 0.01$  mg/L). High levels of fluorides were also sporadically spotted in Mangochi district with the highest value recorded at Nsuya-1 village ( $3.64 \pm 0.01$  mg/L). Maximum pH (9.50

$\pm 0.01$ ) was observed at Mtubwi borehole in Machinga District. There was a general positive correlation between pH and fluoride concentrations in the water samples (Table 1a and b) while no correlation was observed between the fluoride concentrations and electrical conductivity (EC) values. EC is a valuable indicator of the amount of material dissolved in water. Its values fluctuated widely at the different sampled sites. The recommended value of EC for portable water is 2500  $\mu\text{S/cm}$  (WHO, 1988). The high EC values in some water samples (such as 6800  $\mu\text{S/cm}$  at Chigonele in Mangochi district) show that they are unfit for human consumption. The high levels of fluo-ride can largely be attributable to hydrogeochemical origin since anthropogenic factors including disposal of hazardous sewage, liquid and solid wastes from Industries are very insignificant in the sampled rural areas. Therefore, the fluoride concentration depends on the geological, chemical and physical characteristics of the aquifer, the porosity and acidity of the soil and rocks, temperature and the depth of the wells. These are some of the factors that may have to be further investigated in those high fluoride areas if perhaps they can assist in locating alternative sites for planting boreholes or consider defluoridation techniques viable in those areas.

### Use of bauxite for water defluoridation

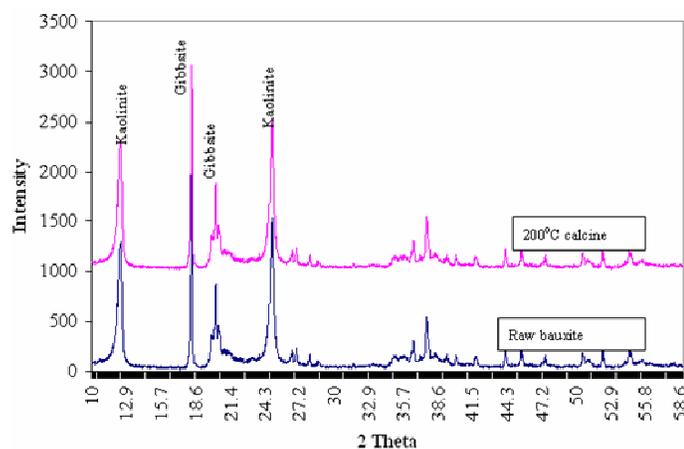
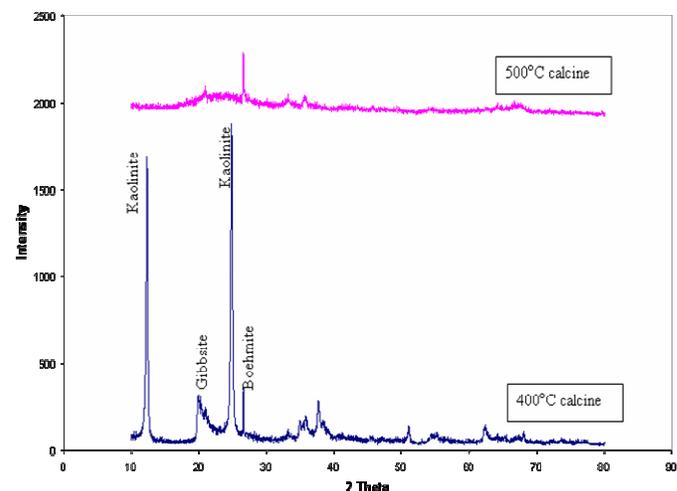
#### Defluoridating material characteristics

The mineralogical characteristics of the bauxite (and its calcined phases) used in this study are shown by the PXRD patterns in Figure 2a and b. The raw and  $200^\circ\text{C}$  calcined phase profiles qualitatively indicate presence of gibbsite ( $\text{Al}(\text{OH})_3$ ) as shown by intense reflection at  $2\theta$  angle of  $17.93^\circ$  ( $d=4.94 \text{ \AA}$ ), and doublet at  $2\theta$  angle of  $20.51^\circ$  probably combining the literature reflections at  $d=4.34 \text{ \AA}$  and  $4.30 \text{ \AA}$  of a crystalline gibbsite. Intense kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) reflections are also shown at  $2\theta$  angles of  $11.58^\circ$  and  $24.80^\circ$ . There are no observable structural changes between the raw and the  $200^\circ\text{C}$  phase. At  $400^\circ\text{C}$  gibbsite has started to transform to boehmite ( $\text{AlOOH}$ ) as can be seen by the loss of its reflections in Figure 2b. However kaolinite shows its high resistance to heat and its reflections are very intense at  $400^\circ\text{C}$  indicating that it becomes more crystalline. Upon calcinations to  $500^\circ\text{C}$  even the kaolinite structure is destroyed resulting in highly amorphous phase that could be attributed to different activated aluminas such as  $\chi$  and  $\gamma\text{-Al}_2\text{O}_3$ . Thermogravimetric results (Figure 3) of the bauxite indicated a very steep mass loss up to  $200^\circ\text{C}$  followed by very small and slow mass loss as the temperature was increased. The first mass loss could be attributable to physisorbed water on the material while the second one could arise from slow dehydroxylation process of the gibbsite as it transforms to different forms

**Table 1a.** Drinking water fluoride concentrations, pH and electroconductivity in suspected fluorosis endemic areas in Southern Malawi (Nsanje, Chikwawa and Mangochi districts)

District	Village/borehole	Fluoride conc. (mg/L)	pH	Electroconductivity( $\mu$ S/cm)
Nsanje	Tengani station	1.32 $\pm$ 0.00	7.22 $\pm$ 0.00	2150 $\pm$ 71
Nsanje	Kaleso vlge/Bangula	<b>1.65<math>\pm</math> 0.06</b>	7.53 $\pm$ 0.00	3150 $\pm$ 71
Nsanje	Bangula market	<b>4.91<math>\pm</math> 0.03</b>	8.65 $\pm$ 0.00	2200 $\pm$ 0
Nsanje	Semba vge	<b>1.89<math>\pm</math> 0.00</b>	7.39 $\pm$ 0.00	3725 $\pm$ 35
Nsanje	Chigumukile	<b>2.45<math>\pm</math> 0.01</b>	7.11 $\pm$ 0.00	3525 $\pm$ 35
Nsanje	Level crossing	<b>7.25<math>\pm</math> 0.01</b>	7.60 $\pm$ 0.00	6600 $\pm$ 0
Chikwawa	Nyamphota/Nkombezi	0.80 $\pm$ 0.01	6.60 $\pm$ 0.00	1700 $\pm$ 0
Chikwawa	Bello vge	0.59 $\pm$ 0.01	7.47 $\pm$ 0.00	1850 $\pm$ 0
Chikwawa	Tomali Admarc	1.02 $\pm$ 0.00	7.57 $\pm$ 0.01	2800 $\pm$ 0
Chikwawa	Tomali Trading Centre	<b>1.91<math>\pm</math> 0.00</b>	8.00 $\pm$ 0.01	2700 $\pm$ 0
Chikwawa	Tomali Dip Tank	<b>1.93<math>\pm</math> 0.01</b>	7.58 $\pm$ 0.00	1450 $\pm$ 0
Mangochi	St. Michael's Sec. Sch.	<b>1.85<math>\pm</math> 0.01</b>	8.05 $\pm$ 0.06	500 $\pm$ 0
Mangochi	Chimbenda vge/Malindi	0.73 $\pm$ 0.01	7.95 $\pm$ 0.07	500 $\pm$ 0
Mangochi	Mlangalanga vge/Malindi	<b>2.60<math>\pm</math> 0.00</b>	6.90 $\pm$ 0.00	990 $\pm$ 14
Mangochi	Mizinga vge	1.50 $\pm$ 0.00	7.00 $\pm$ 0.00	1100 $\pm$ 0
Mangochi	Mtakataka turn off	0.53 $\pm$ 0.00	6.95 $\pm$ 0.07	3100 $\pm$ 0
Mangochi	Matayo vge	0.52 $\pm$ 0.00	7.25 $\pm$ 0.06	2950 $\pm$ 0
Mangochi	MALDECO	0.51 $\pm$ 0.00	8.40 $\pm$ 0.00	500 $\pm$ 0
Mangochi	Mangochi Hospital,	<b>2.45<math>\pm</math> 0.01</b>	6.95 $\pm$ 0.07	1935 $\pm$ 21
Mangochi	Chiwaya vge	1.16 $\pm$ 0.01	6.95 $\pm$ 0.07	1700 $\pm$ 0
Mangochi	Makwinja/Makuzi	1.43 $\pm$ 0.01	7.00 $\pm$ 0.00	790 $\pm$ 0
Mangochi	Mbwadzulu,	0.68 $\pm$ 0.00	7.28 $\pm$ 0.04	3203 $\pm$ 6
Mangochi	Chigonele (Nsauya)	<b>1.85 <math>\pm</math>0.02</b>	7.10 $\pm$ 0.00	6800 $\pm$ 71
Mangochi	Nsangazi F.P. Sch.	1.09 $\pm$ 0.02	7.50 $\pm$ 0.00	2600 $\pm$ 0
Mangochi	Nsauya-1	<b>3.64 <math>\pm</math>0.01</b>	7.00 $\pm$ 0.14	4050 $\pm$ 71
Mangochi	Nsauya/Zimba	0.53 $\pm$ 0.00	7.10 $\pm$ 0.00	1510 $\pm$ 0
Mangochi	Monkeybay Trad. Center	0.55 $\pm$ 0.00	7.50 $\pm$ 0.00	295 $\pm$ 7

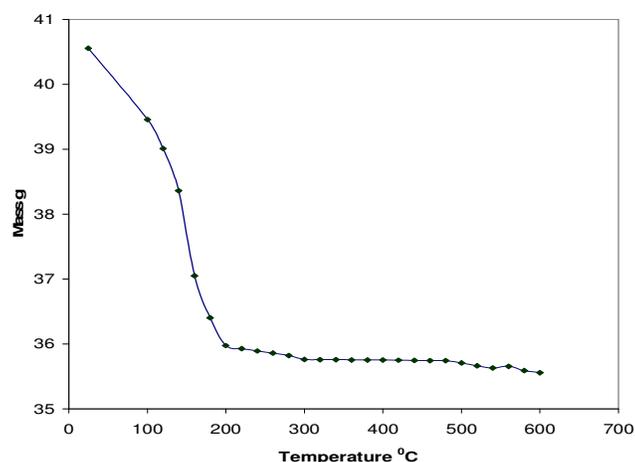
n=3

**Figure 2a.** PXRD profile of the raw bauxite and its 200°C calcined phase used for defluoridation in the study. Gibbsite and kaolinite reflections are indicated within the profile**Figure 2b.** PXRD of 400°C and 500°C calcined phases of bauxite.

**Table 1b.** Drinking water fluoride concentrations, pH and electroconductivity in suspected fluorosis endemic areas in Southern Malawi (Zomba, and Mangochi districts).

District	Village/borehole	Fluoride conc. (mg/L)	pH	Electroconductivity( $\mu$ S/cm)
Zomba	Mapira vge	0.48 $\pm$ 0.00	6.50 $\pm$ 0.00	295 $\pm$ 7
Zomba	Mchilima F.P. Sch	0.58 $\pm$ 0.00	6.30 $\pm$ 0.14	200 $\pm$ 0
Zomba	Chewayile vge	1.24 $\pm$ 0.01	6.90 $\pm$ 0.00	200 $\pm$ 0
Zomba	Tandauko	0.48 $\pm$ 0.00	7.15 $\pm$ 0.21	300 $\pm$ 0
Zomba	Kalolo vge	0.59 $\pm$ 0.00	6.65 $\pm$ 0.07	631 $\pm$ 4
Zomba	Liundi vge	0.26 $\pm$ 0.00	6.95 $\pm$ 0.05	650 $\pm$ 0
Zomba	Chamba School	0.51 $\pm$ 0.01	6.95 $\pm$ 0.07	600 $\pm$ 0
Zomba	Liundi Dada vge	0.45 $\pm$ 0.00	6.95 $\pm$ 0.05	805 $\pm$ 7
Zomba	Milala vge	0.56 $\pm$ 0.00	6.50 $\pm$ 0.00	129 $\pm$ 0
Zomba	Mikunga vge	0.42 $\pm$ 0.00	6.78 $\pm$ 0.22	195 $\pm$ 7
Zomba	Mbando vge	<b>6.51<math>\pm</math>0.01</b>	6.55 $\pm$ 0.07	210 $\pm$ 0
Machinga	Mtubwi B/H	<b>7.51<math>\pm</math>0.00</b>	9.50 $\pm$ 0.00	736. $\pm$ 6
Machinga	Sitola vge	<b>2.76 <math>\pm</math> 0.01</b>	8.55 $\pm$ 0.07	781 $\pm$ 1
Machinga	Chibwana vge	0.24 $\pm$ 0.00	7.55 $\pm$ 0.06	1175 $\pm$ 35
Machinga	Mliwa vge	<b>5.06 <math>\pm</math> 0.00</b>	7.05 $\pm$ 0.07	1050 $\pm$ 0
Machinga	Evangelical Bap. Church	<b>5.08 <math>\pm</math>0.02</b>	8.10 $\pm$ 0.14	580 $\pm$ 0
Machinga	Machinga D.Hospital	<b>4.73<math>\pm</math>0.01</b>	8.15 $\pm$ 0.07	1675 $\pm$ 35
Machinga	Chabwera vge	<b>2.04<math>\pm</math> 0.01</b>	7.90 $\pm$ 0.00	1100 $\pm$ 0
Machinga	Duwa vge	<b>4.88<math>\pm</math> 0.00</b>	8.45 $\pm$ 0.07	750 $\pm$ 71
Machinga	Mombe F.P Scl	1.30 $\pm$ 0.00	7.90 $\pm$ 0.00	80 $\pm$ 0
Machinga	Chedweka	<b>6.47<math>\pm</math>0.01</b>	8.15 $\pm$ 0.07	990 $\pm$ 0
Machinga	Lweya vge	0.28 $\pm$ 0.02	7.70 $\pm$ 0.00	55 $\pm$ 7

n=3

**Figure 3.** Thermogravimetric plot of the raw bauxite.

of alumina ( $\text{Al}_2\text{O}_3$ ).

### Defluoridation capacity and reaction rates

Table 2 presents defluoridation capacities of the different

phases of the bauxite. The highest defluoridation capacity of 95.3% was obtained in defluoridation with the 200 $^{\circ}$ C calcine and this was followed closely by that obtained with the raw bauxite at 94.8%. These two results did not differ significantly at 5% level of significance; as such the calcination is not necessary. The lowest defluoridation capacity of 87.1% was obtained in defluoridation with the 500 $^{\circ}$ C bauxite calcine. The slight increase in defluoridation from raw bauxite to the 200 $^{\circ}$ C calcine could be attributed to absence of physisorbed water that was lost during heating as shown by the thermogravimetric data. The loss of water meant that there was an increase in concentration of the reactive gibbsite and kaolinite for the removal of fluorides. The defluoridation capacities decreased steadily from 300 $^{\circ}$ C through 400 $^{\circ}$ C to the 500 $^{\circ}$ C calcine. This could be a result of phase changes occurring during the dehydroxylation processes. Gibbsite is known to undergo the dehydroxylation sequence gibbsite, boehmite ( $\text{AlOOH}$ ) and  $\chi$ - $\text{Al}_2\text{O}_3$  (about 300 $^{\circ}$ C),  $\gamma$ - $\text{Al}_2\text{O}_3$  (about 450 $^{\circ}$ C),  $\delta$ - $\text{Al}_2\text{O}_3$  (about 800 $^{\circ}$ C),  $\theta$ - $\text{Al}_2\text{O}_3$  (about 900 $^{\circ}$ C) and finally the crystalline  $\alpha$ - $\text{Al}_2\text{O}_3$  commonly known as corundum (above 1100 $^{\circ}$ C) (Sajidu, 2001).  $\gamma$ -alumina ( $\gamma$ - $\text{Al}_2\text{O}_3$ , the phase at 500 $^{\circ}$ C) which can have surface area up to 400  $\text{m}^2/\text{g}$  is an important industrial ca-

**Table 2.** Fluoride concentrations and defluoridation capacities of bauxite and its calcined phase at 2.5 g/200 ml solution of 8 mg/L F<sup>-</sup>

Bauxite phase	Initial Fluoride Conc. (mg/L)	Equil. Fluoride conc. (mg/L)	Fluoride removed (mg/l)	Defluoridation capacity (%)
Raw	8.00	0.42	7.58	94.8
200 °C	8.00	0.38	7.62	95.3
300 °C	8.00	0.77	7.25	90.6
400 °C	8.00	0.90	7.10	88.8
500 °C	8.00	1.03	6.97	87.1

**Table 3.** Correlation coefficients between increase in concentrations and decrease in fluoride concentrations in defluoridation with bauxite

Ion	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>2-</sup>	CO <sub>3</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Ca <sup>2+</sup>	K <sup>+</sup>	Na <sup>+</sup>
Correlation coefficient	-0.23	-0.59	+0.85	-0.07	+0.71	-0.94	-0.17	-0.14

catalyst support needed, for example, in automobile exhaust catalytic converters. The decrease in fluoride uptake as calcination temperature increases therefore suggests that the uptake mechanism is not simple adsorption onto the material surfaces since calcination to 500°C increases the surface area through formation of amorphous alumina phases which would have increased the uptake if adsorption was the only uptake mechanism. It was observed that the pH of the solution increased after defluoridation indicating release of OH<sup>-</sup> ions. This therefore suggests a precipitation mechanism where Al<sup>3+</sup> ions from the material react with the F<sup>-</sup> ion to form stable AlF<sub>3</sub> that precipitate out releasing OH<sup>-</sup> in the process.

The removal of fluoride in this raw bauxite is not only due to gibbsite but also kaolinite. The kaolinite structure includes highly accessible hydroxyl groups positioned on the gibbsite layers which allow for anion exchange modeled in the following equation (Kau et al., 1997):

The insignificant reduction in fluoride removal capacity by the material (95.3% for 200°C calcine to 87.1% for 500°C calcine) could also be explained by the fact that kaolinite is much less prone to desiccation and therefore it is likely that it returns its structure at high temperature and continues to remove the fluoride by almost a constant capacity up to about 400°C of calcinations. At 500°C the bauxite is almost amorphous (without crystalline kaolinite or gibbsite phases). Fluoride uptake mechanism by the 500°C phase can therefore be attributed to adsorption on activated aluminas formed during the calcinations.

The changes in residual fluoride concentrations of the solution mixture (2.5 g of 200°C per 200 ml of 8 mg/L F<sup>-</sup>) as a function of time at room temperature are as shown in Figure 4a. It can be seen from the Figure that fluoride concentration decreases exponentially with time till equilibrium concentration is obtained after 24 hrs of reaction. Therefore we correlated the residual fluoride concentration with time as follows:

$$[F^-] = [F^-]_0 e^{-kt} \quad \text{where } [F^-] \text{ is the residual}$$

concentration at time  $t$  and  $[F^-]_0$  is the initial fluoride concentration which is 8 mg/L and  $k$  is a reaction constant. The following reaction rate equation was applied (Atkins, 1982): for the first order reaction kinetics. A plot of  $\ln[F^-]$  versus  $t$  (Figure 4b) gave a straight line with  $k = 0.1568 \text{ hr}^{-1}$  ( $R^2 = 0.9772$ ) indicating that the reaction is well described by the first order reaction kinetics. The concentration change of the fluoride in this reaction was assumed to be a direct indication of the reaction progress since the concentration change of Al<sup>3+</sup> in both gibbsite and kaolinite was difficult to monitor (due to lack of quantitative characterization of this heterogeneous material). It was also assumed that the bauxite concentration was significantly larger than that of fluoride. The observed kinetics can thus be treated as pseudo-first order kinetics.

In order to determine the maximum dose of the bauxite in a 200 ml solution of 8 mg/L F<sup>-</sup>, different masses of the bauxite were mixed with the solution and the equilibrium residual fluoride concentration was determined. Figure 5 shows that equilibrium concentrations decreased quickly with increase in mass of bauxite used in defluoridation up to about 10g dose. After this point the equilibrium concentrations were within 0.05 to 0.2 mg/L. This implied that increasing the mass of bauxite per volume of water would only increase defluoridation efficiency up to a dose of 10 g/200ml (1 g/20ml)

### Effects of various ions on defluoridation

Table 3 presents correlation coefficients between initial concentrations of various ions in solution and concentrations of fluoride that were attained in solution after deflori-

**Table 4.** Effect of the bauxite on water quality after defluoridation (2.5g of 200°C calcine 200 ml of 8mg/L F<sup>-</sup>)

Parameter	Initial conc.	Conc. after defluoridation	Change in conc.	WHO limit
Al <sup>3+</sup> (mg/L)	0.00	0.13 ± 0.01	0.13 ± 0.01	0.200
SO <sub>4</sub> <sup>2-</sup> (mg/L)	0.00	bdl		400.00
PO <sub>4</sub> <sup>3-</sup> (mg/L)	0.00	bdl		n.a
Si <sup>4+</sup> (mg/L)	0.00	4.11 ± 0.26	4.11 ± 0.26	n.a
CO <sub>3</sub> <sup>2-</sup> (mg/L)	0.00	bdl		500
pH	6.90±0.01	7.4 ± 0.07	0.5±0.07	

bdl: below detectable limits; n.a: not available.

defluoridation. Positive correlation shows that more fluorides remained in solution when the concentration of the particular ion was increased. Negative correlation shows greater fluoride removal as concentration of the particular ion increases. Carbonates and chlorides showed high direct positive correlation indicating that higher initial concentrations of carbonates and chlorides resulted in more fluorides remaining in solution (high concentration of residual fluoride in water). Carbonates and chloride hindered defluoridation with bauxite. The negative effect of carbonates on fluoride sorption could be explained on the basis of comparative solubility of carbonates and fluorides. Carbonates being generally less soluble in water than fluorides interacted more strongly with Al<sup>3+</sup> ions than the fluorides. Chloride hindrance to defluoridation was a result of similarity of chemistry between fluorides and chlorides both ions being halides. General selectivity trends for sorption also place chloride before fluoride ion (NAS, 1998):

Sulphate >iodide >nitrate >bromide >chloride >fluoride  
 Calcium ions showed a high negative correlation indicating a decrease in residual fluoride concentration with increase in calcium ion concentration. Calcium thus enhanced defluoridation and this could be attributable to formation of CaF<sub>2</sub>. Sulphate ions had a moderate enhancement on fluoride sorption a result that contradicts general selectivity trends above. From such a trend sulphate would be expected to interfere with de-fluoridation yet sulphate enhances defluoridation with bauxite. This is in part explained by specific resinion interaction implying that fluoride interact more with bauxite compared to sulphate ion. There exist resin/ion combinations that will not adhere to general selectivity trends (Coulson and Richardson, 1997).

#### Effects of pH on defluoridation

Figure 6 shows defluoridation capacities (2.5g of 200°C calcine in 200 ml of 8mg/L F<sup>-</sup>) at different pH levels. The defluoridation was much lower at pH 2 and pH 10 and optimum pH was obtained at pH 4. The low fluoride uptake at pH 2 could be explained by the greater tendency of fluoride to form aqueous protonated fluoride; thus, reducing the concentration of free fluoride available for

for precipitation with the Al<sup>3+</sup> of the gibbsite or adsorption into the kaolinite layer structure through exchange with OH<sup>-</sup>. At high pH, the lower efficiency could be due to both Le Chatelier's principle and competition. OH<sup>-</sup> and F<sup>-</sup> are isoelectronic with same charge and ionic radii. The higher the concentration of OH<sup>-</sup>, the more difficult it is for OH<sup>-</sup> already attached to Al<sup>3+</sup> to be replaced by F<sup>-</sup> and go into solution. Similar observation has been made by earlier researchers who noted optimum pH of defluoridation by clay minerals at pH 5.8 of the F<sup>-</sup> solution (Moges, 1996).

#### Effects of raw bauxite on water quality

Table 4 shows effects of the raw bauxite on water quality after the defluoridation process. The pH changed from 6.90 ± 0.01 to 7.40 ± 0.07 representing a pH increase by 0.50 unit.

There was insignificant increase in aluminium and silicon in the water. The water quality changes however were within recommended limits (WHO, 2004). The bauxite coloured the water to earth brown making the water unaesthetic for drinking. The colour could easily be clarified by using activated carbons or *Moringa oleifera* seed powder. *M. oleifera* has demonstrated to clarify turbid river water from 500 NTU to 5 NTU (Folkard et al., 1993; Henry et al., 2004).

#### Defluoridation results with actual ground water using the 200°C calcine

Figure 7 gives defluoridation results on water samples collected from high fluoritic sites (Bangula, Level crossing, Mlangalanga, Zimba, Machinga District Hospital and Mtubwi). Batch defluoridation experiments were done on the actual groundwater samples as described for the synthetic fluoridated water above using the 200°C calcined phase of bauxite. The results are consistent with the observations made on the synthetic water. In all cases fluoride concentrations were reduced to below 1.5 mg/L.

#### Conclusion and Recommendations

In expanding the database of fluoride levels in Malawi,

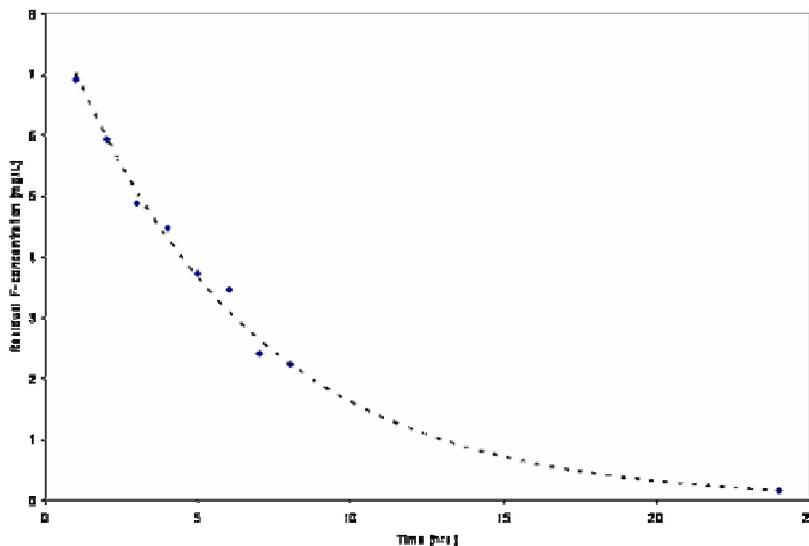


Figure 4a. Residual fluoride concentration against time.

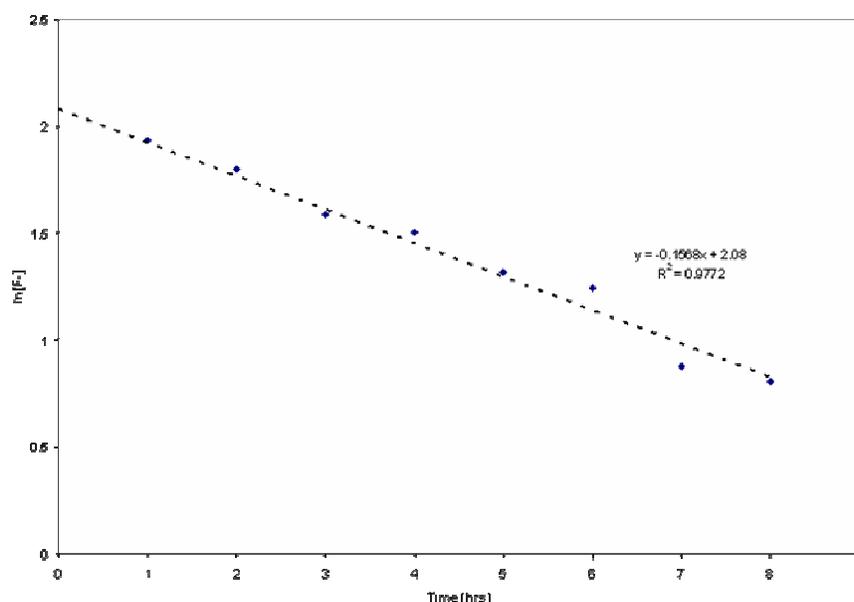


Figure 4b. Plot of  $\ln[F]$  against time.

the work has revealed high levels of fluorides (>1.5 mg/L) in most villages in Nsanje district and in locations around Liwonde in Machinga district. Laboratory experiments have shown the potential of raw bauxite in defluoridation up to 93.8% at a dose of 2.5 g/200ml of 8 mg/L F. This suggests that raw bauxite can be used for defluoridation to treat water in high fluoride areas. The high defluoridation capacity of the bauxite is attributable to gibbsite and kaolinite minerals. Precipitation of  $AlF_3$  is thus predicted to be the fluoride removal mechanism with the gibbsite while exchange of  $OH^-$  groups in the gibbsite layers of the kaolinite with  $F^-$  ions occurs in the kaolinite

component of the defluoridation material. Field trials in a high fluoritic water source such as Mtubwi B/H need to be carried out to test the applicability and efficiency of the method in real life settings.

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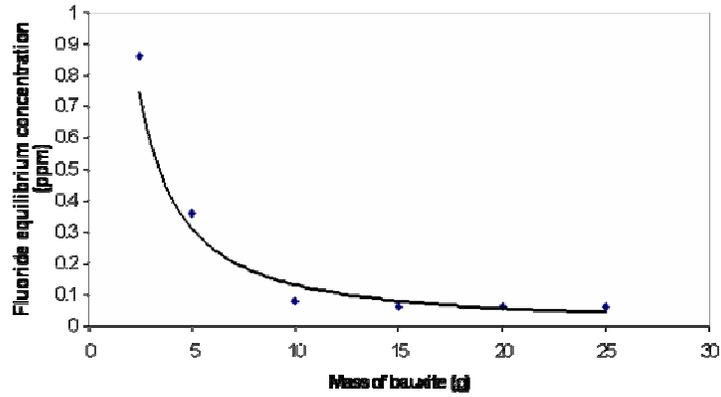


Figure 5. Effects of different amounts of defluoridating bauxite on the fluoride.

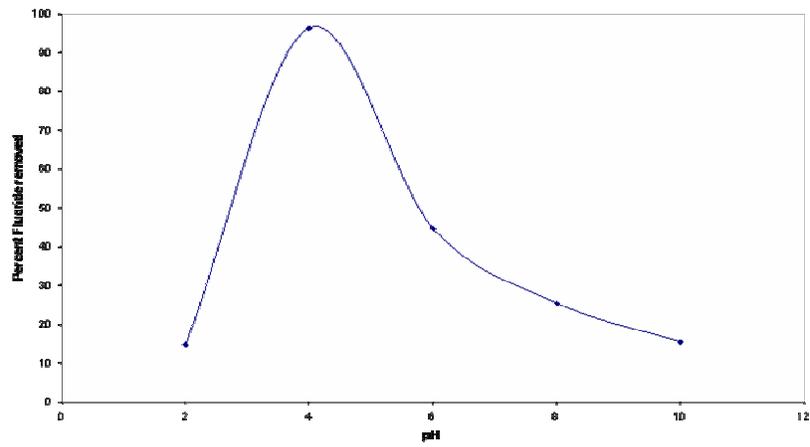


Figure 6. Plot of % fluoride removed versus pH (2.5 g of 200°C calcined phase of bauxite in 200 ml of 8 mg/L F<sup>-</sup>).

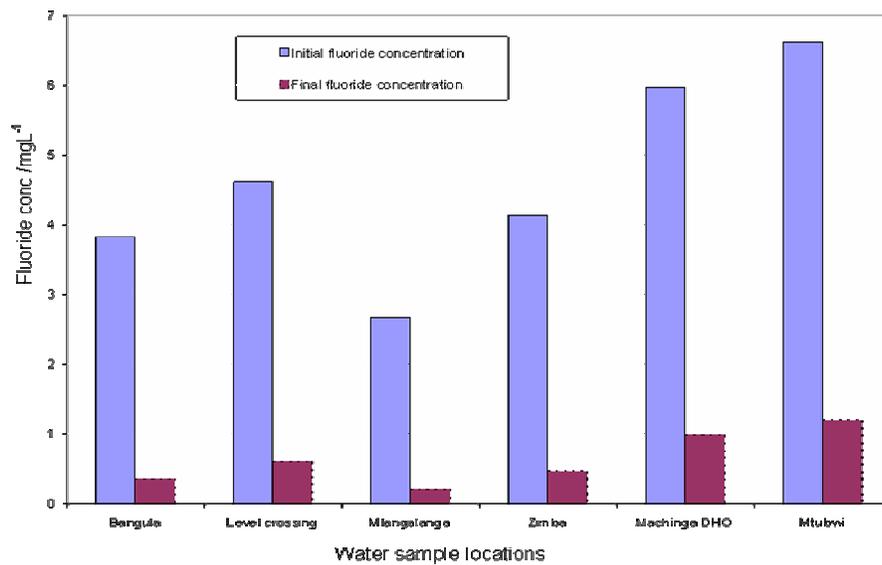


Figure 7. Defluoridation results on water samples.

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