DEFLUORIDATION OF DRINKING WATER BY THE USE OF CLAY/SOIL

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SUMMARY: The present is part of a greater project assessing the fluoride-binding effect of soils from different parts of the world. In this part the clay/soil samples from Ethiopia are studied with respect to capacity and the effect of heating and stirring. The F-binding capacity of an «optimal» soil sample, laterite from Northern Cameroon is assessed by the use of sequential filtration. Five soil samples, collected from the high-land areas around Addis Ababa, reduced the fluoride content of the water from about 15 to 1 mg/L, at dosage levels of about 100 g/L. Pre-drying at 50 ºC resulted in similar efficiency as preheating at 250°C. Soil samples from high-fluoride areas of the Ethiopian Rift Valley showed much lower and even negative removal efficiencies. Stirring speeded up the process, but it did not influence the finally obtained removal capacity. A gradual decline in F-removal efficiency was seen in the laterite used for sequential filtration. The average removal efficiency under the selected sequential filtration conditions was about 58 %, ranging from 90 % during the first sequences down to practically nil in the 30th runs. With an initial fluoride concentration of 15 mg/L, the total fluoride binding capacity of laterite from Cameroon was found to be approximately 0.5 mg/g. It is concluded that the high-land soil, due to easy availability and low cost, may be useful for removal of excessive fluoride from drinking water at household and village levels.

Key words: Fluoride removal; Lateritic soils; Clay firing; Stirring; Fluoride binding capacity; Ethiopian soil.

INTRODUCTION

Harmful effects of fluoride intake are primarily, but not exclusively, linked to high levels of fluoride in the drinking water. As high-fluoride groundwater is often the only available and reliable source of water in low-precipitation fluorotic areas such as the East African Rift Valley, simple methods for low-cost defluoridation of drinking water are urgently needed.[1]

A series of methods have been suggested for the defluoridation of drinking water, but the *ideal system* may not yet have been found. Any health measure should, in order to be implemented, be effective, inexpensive and simple, and also *socially and ethically acceptable*. Thus, well-known, locally available defluoridation media such as clay and soil are of much interest in the high-fluoride areas of East Africa.

Fluoride is a natural constituent of the biosphere, and, consequently, of clay and soil. The inherent fluoride content, however, varies greatly from one area to another. Geology as well as the local topography[1] and depth of the soil layer[2] are factors to be considered in the quest for soils suitable for defluoridation purposes.

Clay-pots have, especially in the past, been widely used for the transport and storage of drinking water. Inexpensive, locally made ceramics may improve the quality of the water: apart from keeping water relatively cool, the clay pots may reduce the fluoride content of the water.[3] The fluoride binding effect of clay-ware is influenced by factors such as physico-chemical composition of the clay and the firing temperature in the kiln.[4] The aim of the present study was:

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- to assess the fluoride binding effect of various Ethiopian soils, sampled, respectively, in mountainous and (relatively) low-land areas of the Rift Valley
- to test the possibility of using low-fired soils or soils with no previous firing for defluoridation of drinking water
- to study the effect of *stirring,* and, finally
- to assess the fluoride binding capacity in an «optimal» soil, laterite from Northern Cameroon, West Africa.

Findings related to the relative elevation of soil samples are more specifically reported elsewhere.[5] Here are presented results concerning preheating of the soil, stirring/no stirring of the water/soil systems, and also findings regarding the fluoride binding capacity of lateritic soil samples from Cameroon.

MATERIALS AND METHODS

Soil samples. Ten topsoil samples (mostly red, lateritic clay) were collected in Ethiopia. Four of them, i.e. no 1 – 4, were from the mountainous areas around Addis Ababa. The six others, i.e. no 5- 10, were from the high-fluoride areas of the Rift Valley. In addition, samples of lateritic soil were collected from the high-land savannah of Adamoua, Northern Cameroon.

Pre-treatment. The Ethiopian samples were heated for about 3 hours at 250°C in an electrical furnace. Alternatively the samples were dried at 50°C for a similar period of time. Aliquots of 30-45 g were prepared from each of the soil samples. The Cameroon samples were left unheated.

Fluoride water. Fluoride solutions were prepared by dissolving 100 mg NaF in 3.0 L distilled, de-ionised water, giving a fluoride concentration of approximately 15 mg/L. Alternatively groundwater containing 7.4 mg F/L and NaF solutions containing 8.7 mg F/L were used.

Batch kinetic experiments. Soil samples were added to plastic containers and mixed with fluoride solutions in a weight/volume ratio of 1:10. The containers were closed by tight-fitting lids and placed on an electrical shaker (50 motions/min). At given different contact times, 5 mL samples were taken and analysed for the residual fluoride concentration in the water.

Capacity measurement. 100 g of untreated laterite was placed in a funnel - on filter paper circles - and used for sequential filtration of 4.8 L of the 15 mg F/L NaF solution described above. The filtration was carried out sequentially, where 200 mL aliquots were filtered at a time in total 24 times. The fluoride concentration was measured in each of the 24 filtrates. Three parallel test series were conducted.

Fluoride measurements. The fluoride concentrations were measured by the use of an Orion combination F^- electrode (9600900) connected to an Orion Research microprocessor ionalyzer/900.

RESULTS

Various soils. A sharp decline in the fluoride concentration was seen in all NaF solutions exposed to soils from the Ethiopian highlands. During the first hour roughly 50 % of the fluoride ions were removed from the water samples (Figures 1 and 2). In 24 hours the fluoride concentration was reduced to about 1 mg/L in all the four samples.

Only minor differences were observed in the fluoride binding patterns of soils fired at 250°C as compared the similar patterns of soils heated to 50°C only (Figure 1 versus Figure 2).

The fluoride removal effect of the soils from the Rift Valley was very limited; the average fluoride concentration in solutions after 24 hours of exposure was 10.5 mg/L, individual samples varying from 4.85 to 15.9 mg F/L; the last soil sample actually causing an increase in the fluoride content of the NaF solution (Figure 3).

Effect of stirring. The effect of stirring on fluoride removal in natural and artificially made high-fluoride waters was tested in medium efficient Ethiopian soil samples. As demonstrated by Table 1, stirring speeded up the initial fluoride binding process, but did not alter the efficiency on long-time. The fluoride removing effect, given in percentage of original fluoride concentration, was similar in artificial and naturally occurring high-fluoride waters.

Fluoride binding capacity. A sharp reduction in fluoride concentration was observed in water passing through the column made up of laterite from Cameroon. During the first few runs, the reduction was approximately 90 %. A gradual decline in the effect of filtration took place, but even after the 18th filtration, i.e.3600-mL of water containing 14.7 mg F/L, more than 50 % of the fluoride was removed by the laterite, cf. Figure 4.

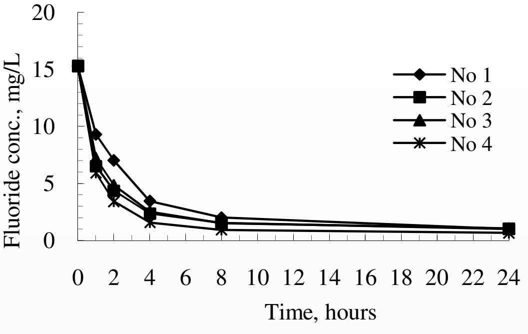

FIGURE 1. Defluoridation of water by the use of soil from the Ethiopian highland. The soil was heated at 250°C for three hours. The dosage was 10 g/L.

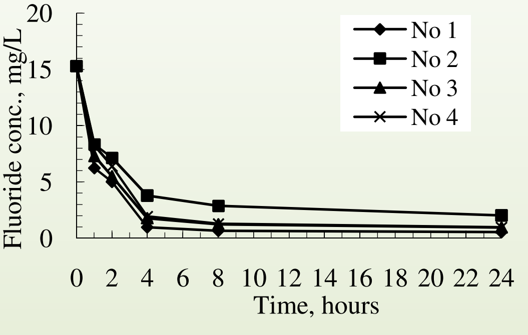

FIGURE 2. Defluoridation of water by the use of soil from the Ethiopian highland. The soil was used without heating. The dosage was 10 g/L.

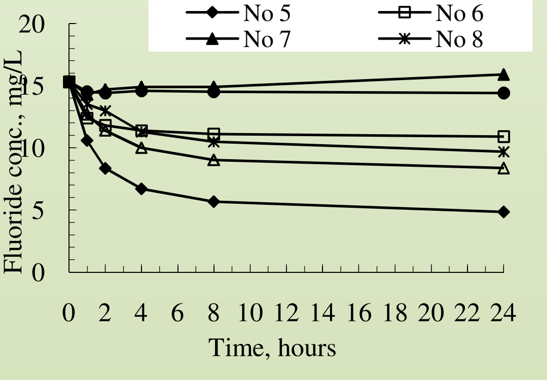

FIGURE 3. Defluoridation of water by the use of soil from the Ethiopian Rift Valley. Heated for three hours at 250°C. Dosage 100 g/L.

TABLE 1. Defluoridation by the use of laterite, in artificially made high-fluoride, respectively naturally occurring waters, with or without stirring. Results given in percentage of original fluoride

concentrations 8.7 mg F/L, respectively 7.4 mg F/L.

Type of water	Stirring	Fluoride removal in % after exposure time				
		2 h	4 h	8 h	24 h	7 days
NaF solution	Yes	48.7	64.4	77.6	87.2	94.0
NaF solution	No	19.2	25.4	40.7	65.2	95.0
Groundwater	Yes	50.3	66.8	76.4	84.2	93.0
Groundwater	No	25.9	32.7	44.1	50.0	93.0

The experiment was terminated after 24 runs. By extrapolation one should expect the laterite filter (100 g) to be saturated by fluoride after approximately 6 more runs, i.e. after the filtration of 6000 L of fluoride solution containing 14.7 mg/L. The average removal of fluoride in the water would then be indicated in the graph as the adsorption of the 15th aliquot, i.e. 8.5 mg/L. Thus the trend shows that 100 g laterite may take up not less than 50 mg of fluoride, at an average removal efficiency of 58 %. The binding capacity, under such conditions would be slightly more than 0.5 mg/g.

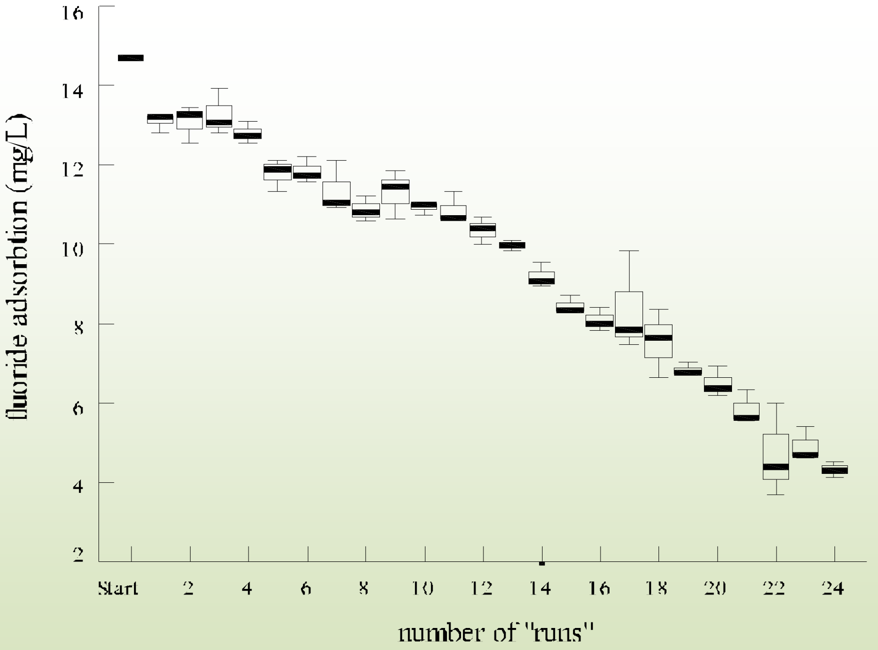

FIGURE 4. Box plot demonstrating the gradual reduction of fluoride binding effect in a laterite filter, after repeated exposure to aliquots of 14.7 mg/L NaF solutions. Experiment made in triple.

DISCUSSION

The fluoride which enters the hydrological system may, to a large extent, be traced back to volcanic activities associated with rift formation and chemical weathering of volcanic rocks.[6] The African Rift System is dominated by alkaline base-rocks, richer in Na and F than analogous rocks in other regions of the world[7], and high-fluoride groundwater is a rule, rather than an exception in the Rift Valley. Dental and skeletal fluorosis, consequently, are endemic in the region and there is an acute need for simple and inexpensive methods for defluoridation of water.[8]

Clay pots, made from the local clay, have been tested for fluoride removal e.g. by Ndegwa.[3] Most writers have concluded that the method is too slow and that clay-ware has too little fluoride removing capacity.[9] As shown in our experiments, however, the capacity and the speed depend on the selection of clay/soil, and on the practical procedures involved in the fluoride removing process.

Recently, Zewge and Moges[10] investigated brick and pot chips as defluoridating media, and reported fluoride binding capacities up to 0.56 mg/g, which is similar to what we found in our column studies. This is still a ***low*** capacity, as compared to *ando soil,* a relatively young, black soil prevalent e.g. in Kenya[11] or *contact precipitation with sodium dihydrogen phosphate and calcium chloride*, as described by Dahi.[12] However, lateritic clay in most places is available at practically no cost, and by the use of simple batch-type methods drinking water with an acceptable fluoride concentration may be provided in less than 24 hours. By the use of stirring, the fluoride binding process may be speeded up. Likewise, a columnar type of soil/clay filter may produce low-fluoride water rather quickly.

Firing sterilises the clay, and reduces the turbidity induced by the defluoridation process. From an environmental point of view, however, firing should be avoided, as it requires energy and may lead to further deforestation and ecological strain in vulnerable areas such as the East African Rift Valley. Our finding that no firing of the soil is needed for defluoridation purposes would seem to make the proposed method even simpler. However, the possibility of micro-biological contamination of the soil, and, consequently, of the drinking water, should not be overlooked. Further studies are needed to assess this aspect.

Most of our experiments have been conducted using artificially made NaF solutions. According to the results presented in Table 1, defluoridation of, respectively, NaF solutions and chemically more complicated high-fluoride groundwater, seems to follow the same pattern.

Lateritic soils may not be «best» solution to the treatment of high-fluoride waters. Soil is, however, easily available in the problem-areas, the method is socially and environmentally acceptable, and implementation requires a minimum of equipment and technical skill. Even with its relatively low fluoride binding capacity, 1 kg of laterite should - according to our findings - be able to reduce the fluoride content of 100 L water from, e.g. 6 mg/L to less than 1 mg/L. Hence, the use of local clay or soil could possibly represent a simple and inexpensive way of improving the quality of drinking water in high-fluoride areas; at household level and at village level.

ACKNOWLEDGEMENT

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