Fluoride Release from the Weathered Rocks in Chronic Kidney Disease of Unknown Etiology Endemic Regions in Sri Lanka

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Abstract - Fluoride is recognized as one of the risk factors for Chronic Kidney Disease of unknown etiology (CKDu) due to its high prevalence. Studies regarding the leaching behaviour of fluoride from rocks in CKDu prevalent areas is scarce. Therefore, this study is focused on identifying the behaviour of fluoride release from a weathered rock commonly found in CKDu endemic area (Girandurukotte) and compare with a CKDu non-endemic area (Sewanagala). Weathered rocks were collected at 5 m depth from freshly excavated subsurface wells. Mineralogy of the rocks was analysed using X-ray diffraction method. Alkaline digestion using KOH been carried out to determine the total fluoride content in rocks. Fluoride leaching experiments were conducted to determine the kinetics of the fluoride release into groundwater and a sequential extraction to determine the fluoride fractions in rocks. Quartz, biotite, carbonate fluorapatite and gypsum were found as primary minerals in the rock from Girandurukotte while quartz, biotite, albite and feldspar were found in the rock from Sewanagala. Total fluoride content found using alkaline digestion was higher in the rock from Girandurukotte (994.8 mg/kg) compared to Sewanagala (788.1 mg/kg). According to fluoride leaching, a higher concentration of fluoride being leached from the rock from Sewanagala (6.81%) compared to Girandurukotte (2.60%) with HCO_3^- rich water. Based on the sequential extraction data, the rock from Sewanagala (10.19 mg/kg) found to have more fluoride in the exchangeable fraction compared to Girandurukotte (4.40 mg/kg) concluding that the rock from CKDu non-endemic area got more ability to release fluoride into groundwater.

Keywords: Fluoride, Weathered rock, Groundwater, Kidney disease

I. Introduction

Hofmeister series is a classification of cations and anions which Franz Hofmeister ranked based on their capacity to denature proteins [1]. The ranking is protein specific, but a typical Hofmeister series is: Cations: $NH_4^+ > K^+ > Na^+ > Mg^{2+} > Ca^{2+}$; Anions: $F^- > H_2PO_4^- \geq SO_4^{2-} > HCO_3^- > Cl^- > NO_3^-$. The strong protein denaturing ability of fluoride makes it one of the most active ions in this Hofmeister series. The prolonged exposure of the kidney to many Hofmeister ionic species, all below maximum allowed limits (MALs), but adding to a high ionicity which is termed 'chronic exposure' may have led to an emergence of a new form of chronic kidney disease (CKD) of unknown. Due to impaired kidney function of an unknown reason; this was named 'chronic kidney disease of unknown etiology (CKDu) by the World Health Organization [2]. CKDu is responsible for tens of thousands of deaths every year in Sri Lanka, and it has become a significant burden on public health and health care systems.

The Hofmeister ions occur naturally in rocks and the water-rock interaction plays a major role in their release into groundwater. When rocks are exposed to the weather agents, a series of chemical processes start and these chemical processes lead to the alteration of the rock minerals and the release of fluoride and other Hofmeister ions. Intense weathering of rocks, and minerals, and passage of some chemical species into the aqueous medium enhance the entry of these ions making long residence the main cause of enhanced ionicity in groundwater [2]. Accumulation of Hofmeister ions including fluoride in drinking water sources, and prolonged use of subsurface groundwater with high ionicity may contribute to CKDu by a protein denaturing mechanism in the kidney [1]. According to the World Health Organization (WHO), the permissible fluoride content in water is 1.5 mg/L. However, the optimal concentration of fluoride can vary according to climatic conditions. Recommended limits for fluorides in drinking-water ranged from 0.6–0.8 mg/L for tropical regions having daily air temperatures between 26.3–32.6°C. A recent study carried out in Girandurukotte found that 0.02-2.14 mg/L of fluoride with an average of 0.64 mg/L in groundwater [3]. Prolong exposure to high fluoride concentrations through drinking groundwater gained a lot of attention with regard to the incidents of CKDu in Sri Lanka. Therefore, this study is focused on identifying the release of fluoride from weathered rocks in the CKDu endemic region and compare with the same in CKDu non-endemic region.

II. Materials And Methods

A. Methods

Study area description. This study was carried out in Girandurukotte, a CKDu endemic area, and Sewanagala, a CKDu non-endemic area both belonging to the dry zone low country region. Annual rainfall is around 1,800 mm, mainly from October to December, and the average temperature is about 30°C (29°C–30°C).

Sample Collection. A total of two partially weathered rock samples were collected from a depth of 5 m from two fresh

excavated wells from CKDu endemic (Girandurukotte) and CKDu non-endemic (Sewanagala) regions.

Characterization of rock samples. X-ray diffraction (XRD) analysis was done using Seimens D-5000 Diffractometer for the rock samples to understand the mineral composition. The XRD data was obtained in the 2θ range from 3 to 60° (Step width: 0.02°; scan speed/duration time: 4.000°/min) for samples.

Total' fluoride in the rock samples. A total of 0.5 g of prepared rock sample was weighed accurately up to 4 decimal places into nickel crucibles and 2 ml of 50% (w/v) potassium hydroxide solution was added. Thorough mixing was achieved by gently shaking the crucibles, followed by heating on a hotplate calibrated to 100°C for 30 min. The crucibles were heated in a muffle furnace until reaching 600°C and then holding for a further 30 min. Cooled samples were filtered through 0.45 µm cellulose nitrate filters. Samples were analysed by ion chromatography (IC) (Metrohm-930 Compact IC Flex).

Leaching kinetics with HCO_3^- rich water. A volume of 20 ml of prepared 150 mg/l $NaHCO_3$ solution was transferred into each 5 g of the rock sample and mixed well. A sample volume of 2.5 ml was collected at 60 min, 120 min, 240 min, and 480 min, 1 day, 2 days, 4 days, and 8 days and analysed the dissolved fluoride in the leach liquor using IC method.

Sequential Extraction experiments of the weathered rock samples. Step-wise sequential extraction was carried out to assess exchangeable, carbonate bound, Fe-Mn oxide bound, organic matter bound and residual fractions of fluoride [4].

III. Results And Discussion

Rocks from both CKDu endemic and non-endemic areas were biotite gneiss in type. According to XRD data, quartz, biotite, carbonate fluorapatite and gypsum were found as primary minerals in the rock from CKDu endemic area while quartz, biotite, albite and feldspar were found in the rock from CKDu non-endemic area. Total fluoride content found using alkaline digestion was higher in the rocks from CKDu endemic area (994.8 mg/kg) compared to CKDu non-endemic area (788.1 mg/kg). According to the fluoride leaching kinetic experiments carried out for 8 days in HCO_3^- rich water, a higher concentration of fluoride being leached from the rock from CKDu non-endemic area (6.81%) compared to CKDu endemic area (2.60%) with HCO_3^- rich water (Fig. 1). Higher amount of exchangeable fluoride in the rock from CKDu non-endemic region could be a reason for this variation.

Furthermore, based on the sequential extraction data (Table 1), higher fluoride content was found in the residual phase in both rocks collected from CKDu endemic (88.63%) and non-endemic (92.41%) areas. The rock from CKDu non-endemic area (10.19 mg/kg) found to have more fluoride in the exchangeable fraction compared to the rock from endemic area (4.40 mg/kg). Fraction of fluoride bound to organic matter as well as to Fe-Mn oxide were remained higher in CKDu endemic area (6.45 and 4.28% respectively) compared to non-endemic area (4.21 and 1.94% respectively) while the fraction of fluoride bound to carbonates was higher in CKDu nonendemic area (0.22%) compared to endemic area (0.15%).

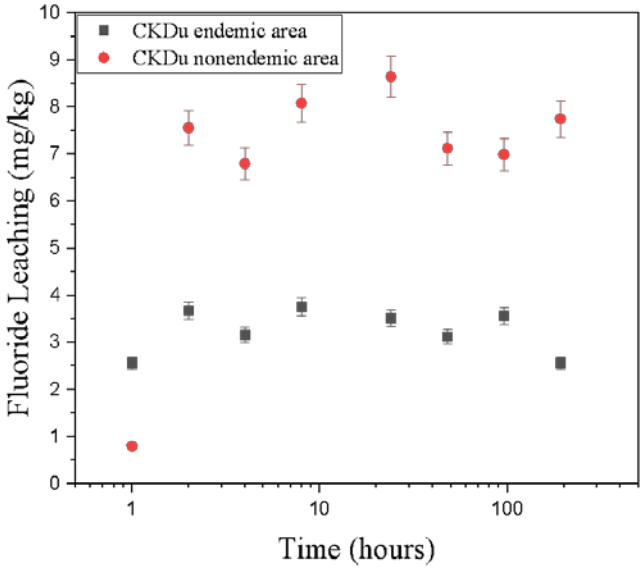

Fig. 1 Fluoride leaching kinetics of powdered rock samples collected from CKDu endemic and non-endemic areas with HCO_3^- rich water

Table 1: Amount of fluoride bound in different phases of the two rock samples collected from CKDu endemic and non-endemic areas

Phases	Fluoride content of the rock samples	
	CKDu endemic area (mg/kg)	CKDu non-endemic area (mg/kg)
Exchangeable	4.403	10.20
Bound to carbonates	1.514	1.776
Bound to Fe-Mn oxide	42.63	15.29
Bound to organic matter	64.55	32.53
Residual	881.7	728.3
Total fluoride	**994.8**	**788.1**

IV. Conclusion

This study demonstrates that the rock from CKDu non-endemic area (Sewanagala), contain high amount of fluoride in the exchangeable phase compared to the rock from CKDu endemic area (Girandurukotte) proving the fluoride leaching behaviour of the rock from CKDu non-endemic area having higher capacity in releasing fluoride into water.

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