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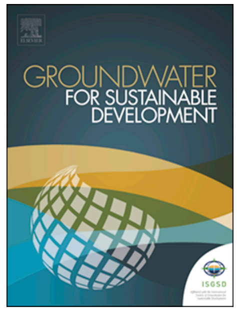

Geogenic fluoride and arsenic in groundwater of Sri Lanka and its implications to community health

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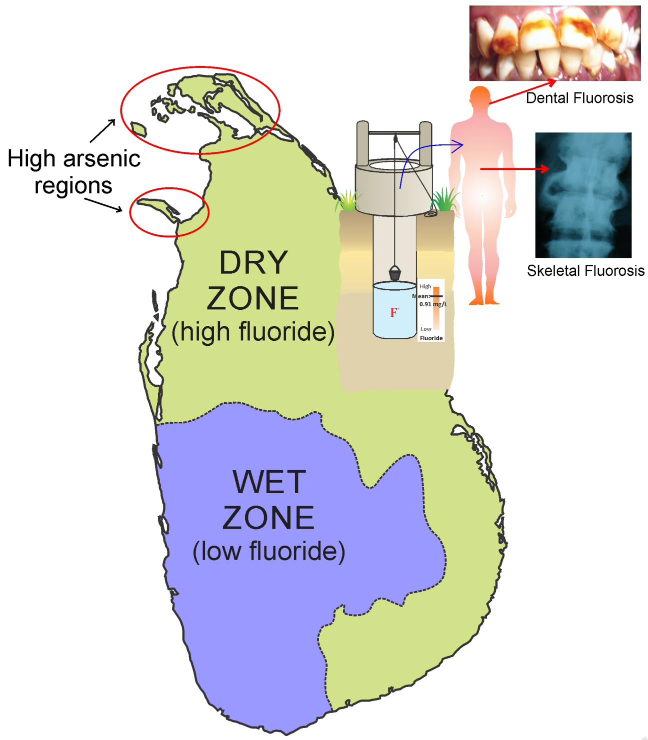
High arsenic regions
DRY ZONE (high fluoride)
WET ZONE (low fluoride)
Dental Fluorosis
Skeletal Fluorosis

Geogenic fluoride and arsenic in groundwater of Sri Lanka and its implications to community health

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Highlights

- Fluoride and arsenic dissipation in the groundwater in Sri Lanka is reviewed.
- Groundwater in dry regions show elevated fluoride levels causing dental and skeletal fluorosis
- Introducing a household level defluoridating method is required for the high fluoride regions.
- Naturally occurring groundwater with high As (>10μg/L) is recorded in sedimentary aquifers.

ABSTRACT

Fluoride and arsenic in groundwater are two of the most discussed elements in the emerging science "Medical Geology". This paper reviews the studies conducted during the last 30 years in Sri Lanka on fluoride and arsenic in groundwater. These studies have clearly indicated that several regions of the dry zone of Sri Lanka are affected by excessive quantities of fluoride in the groundwater. Apart from the well-known dental fluorosis, skeletal fluorosis was also reported up to a certain extent in the high fluoride regions. The recent increase in the incidence of chronic kidney disease of unknown etiology (CKDu) has also highlighted the importance of the geochemistry of fluoride in groundwater of the dry zone. Although geologically, the dry zone of Sri Lanka does not differ markedly from the wet zone, the climate and the hydrological conditions play a significant role in the geochemistry of fluoride and its impact on human health. Over 50% of wells in the dry zone regions of Sri Lanka have fluoride levels higher than 1.0 mg/L while the fluoride content is also higher in deep wells compared to the shallow wells. Arsenic in groundwater is not yet considered as a serious issue in Sri Lanka, particularly in aquifers in the metamorphic terrain, but higher arsenic levels were recorded in sedimentary terrains. The toxicity effects of high arsenic in such terrains still remain a neglected health concern that needs greater attention. Since high fluoride is a major problem in the dry zone regions with severe health concerns, suitable defluoridation methods need to be introduced at the household level.

Keywords: CKDu; dental fluorosis; skeletal fluorosis; dry zone; sedimentary aquifers, health hazards

INTRODUCTION

The relationships between the natural environmental factors and the health of the inhabitants in a terrain have been known for centuries. Exposure, either to lower or higher levels of certain chemical constituents through drinking water, food or air leads to numerous non-communicable diseases. The science dealing with the relationship between natural geological factors and health of man and animals, now defined as "Medical Geology" describes the influence of ordinary environmental factors on the geographical distribution of health problems (Dissanayake and Chandrajith, 1999; Finkelman et al., 2018; Finkelman et al., 2001; Selinus, 2002). Such health issues are more apparent in the tropical equatorial belt, where the vast majority of countries are less developed, compounded by economic, health, agricultural and many other issues. Geogenic and climatic factors are also unique in these terrains and are further compounded by the fact that their human populations are exceedingly high. Tropical countries are very often subject to a variety of geogenic disasters, including problems relevant to water quality and health issues (Bundschuh et al., 2017). In such terrains, water stress and water quality issues are more severe and expected to increase in the near future with the predicted climate change impacts (Kundzewicz et al., 2008). Providing safe water to the community is one of the important considerations in the Sustainable Development Goals (SDGs), and assessing water quality is therefore , an important consideration in providing potable water for the community (Alcamo, 2019; Bundschuh et al., 2017; Li and Wu, 2019; Yunus et al., 2019), Most importantly in these terrains, groundwater is very often used as drinking water directly with no purification, and the link between groundwater chemistry and health becomes obvious. Therefore, from a medical geology perspective, groundwater geochemistry is of special importance.

The groundwater derives its solutes from contact with various solids, liquids, and gases as it finds its way from the recharge to the discharge area. The chemical composition of the rocks, minerals, and soils through which the groundwater flows causes very large variations in the geochemistry of the groundwater (Dissanayake and Chandrajith, 1999; Finkelman et al., 2018). In most developing countries in the tropical equatorial belt, contamination of water due to industrial emissions are minimal and the chemistry of the rocks, minerals, and soils of a terrain is of paramount importance for the geochemistry of groundwater and hence the health of the indigenous populations. The anomalous levels of certain dissolved constituents would undoubtedly impact the health of the people living in an area.

Since the quality of drinking water has a clear impact on public health, the World Health Organization (WHO) imposed guidelines and standards for many of these constituents including elements and other harmful substances. One of the important aspects of the essentiality of elemental constituents is the margin between individual and population requirements and the tolerable intake. Developing countries with their different lifestyle patterns and inadequate nutritional supplements coupled with a host of natural and anthropogenic environmental problems may have markedly different tolerable intakes as compared to those living in developed and temperate countries. Therefore, the relationship between water quality and human health is more apparent in developing countries where centralized water supply systems are not available (Dissanayake and Chandrajith, 2007; Li and Wu, 2019). In developed countries where centralized water supply systems are freely available, water quality can be regulated and monitored, and proper standards are maintained.

From among many other relationships between geochemistry of human health, the link between fluoride and arsenic geochemistry of drinking water in an area and incidences of health effects are very well-established in medical geology. During the last few decades, several studies had been carried out throughout the world to investigate the geochemical relationship of fluoride and arsenic and the health of populations. The aim of this paper is to review some recent studies on the geochemistry of fluoride and arsenic in groundwater and their health impacts, giving particular emphasis to the tropical terrain of Sri Lanka.

FLUORIDE AND HUMAN HEALTH

Fluoride in drinking water becomes a serious problem globally, since nearly 200 million people, mostly from tropical countries, are vulnerable to dental and/or skeletal fluorosis (Figure 1)(Kimambo et al., 2019). Fluoride related health issues were noted in many counties like China (Guo et al., 2014; Wen et al., 2013), India (Ali et al., 2019; Jacks et al., 2005; Reddy et al., 2010; Saxena and Ahmed, 2003; Yadav et al., 2019); Pakistan (Rafique et al., 2009; Rasool et al., 2018); eastern African countries (Davies, 2003; Gaciri and Davies, 1993; Kut et al., 2016), Sri Lanka (Balasooriya et al., 2019; Chandrajith et al., 2012; Dissanayake, 1991, 2005; Ranasinghe et al., 2019; Wickramarathna et al., 2017), Mexico (Armienta and Segovia, 2008; Daesslé et al., 2009; Valenzuela-Vasquez et al., 2006); Argentina (Gomez et al., 2019; Gomez et al., 2009; Kruse and Ainchil, 2003) among others, have very high incidences of dental and in many cases skeletal fluorosis mainly caused by the excess fluoride in drinking water (Ali et al., 2019; Dissanayake, 1991, 1996; Edmunds and Smedley, 2013).

Fluorine is one of the most abundant elements in the geogenic environment and occurs ubiquitously in natural water as its ionic form fluoride (Ali et al., 2016). Although fluoride could be considered an essential element for human health in low doses, excessive fluoride has detrimental effects on health. While the essentiality of fluoride for human health is still being debated, its toxicity has now caused considerable concern in many regions where fluoride is found in excessive quantities in their drinking water. However, the optimum range of fluoride varies within a very narrow margin causing fluoride imbalances, often in populations in tropical countries where people consume large quantities of water with higher fluoride levels. With most trace elements required by man, food is the principal source, but fluoride enters the human body from water (Dissanayake and Chandrajith, 2019). Most importantly, the essentiality and toxicity of fluoride are divided by a narrow line. The WHO recommended drinking water standard for fluoride is 0.5 to 1.5 mg/L (WHO, 2011).

Fluoride is an important element for the homeostasis of bone mineral metabolism (Dissanayake and Chandrajith, 2007). Due to the chemical similarity of fluoride and hydroxyl ions, ingested fluoride is strongly adsorbed on mineralized tissues of the body which are composed mainly of the mineral hydroxyl apatite [$Ca_5(PO_4)_3OH$]. Over 90% of fluoride in the body is retained in the skeleton and teeth (Ali et al., 2016; Ghosh et al., 2013). Soft tissues do not generally take up fluoride except by the pineal gland where fluoride accumulates in excessive levels (Luke, 2001; Malin et al., 2019). Bones are constantly resorbed and re-deposited during a lifetime, and high fluoride can affect the Ca-turnover rates of bone.

Dental fluorosis occurs as a result of exposure to excess fluorides during the childhood, particularly during the age of teeth formation, developing at levels above 1.5 mg/L (Ali et al., 2019; WHO, 2011). As a result, enamel becomes harder and discoloured. Although dental fluorosis does not affect the tooth as such, noticeable cosmetic effects can appear in teeth (Figure 2). Long term and continuous exposure to a high level (>4 mg/L) of fluoride leads to hardening of bones, joint pain and limb motor dysfunction known as skeletal fluorosis (Dissanayake and Chandrajith, 1999; Zuo et al., 2018). Extreme chronic exposure of environmental fluoride could cause crippling fluorosis. Choubisa (2001) noted that crippling fluorosis can appear at exposures even at about 2.8 mg/L of environmental fluoride with an extreme form of skeletal fluorosis known as kyphosis and genu varum, in some cases particularly among adults over 45 years of age (Choubisa and Choubisa, 2019). Patients with skeletal fluorosis with spinal cord compression were also reported in the dry zone of Sri Lanka due to the regular consumption of high fluoride water for about 20 years (Dissanayake, 1996). In addition to health issues of hard tissues, chronic exposure to high levels of environmental fluoride could affect the functions of liver, kidney, heart, lungs, brain, thyroid gland, chromosomes, nervous systems development and reproductive abilities (Kumari and Kumar, 2011; Nakamoto and Rawls, 2018; Zuo et al., 2018). Chronic exposure of fluoride for prolonged periods possibly causes osteosclerosis and end-stage renal failure leading to chronic kidney diseases in certain tropical equatorial regions (Balasooriya et al., 2019; Chandrajith et al., 2011a; Dissanayake and Chandrajith, 2019;

Lantz et al., 1987). Harinarayan et al. (2006) have also shown evidence of chronic fluoride intoxication associated with renal tubular dysfunction that leads to both bone and kidney disease. The importance of fluoride as a geochemical marker for Chronic Kidney Disease with unknown etiology (CKDu) in Sri Lanka was discussed by Dissanayake and Chandrajith (2017) and Dissanayake and Chandrajith (2019). Damaged kidneys accumulate more fluoride, resulting in further damage to kidney, bone and other organs (Connett, 2012).

Health effects of fluoride have been observed even at lower levels than the WHO recommended levels, particularly in tropical terrains (Ghosh et al., 2013; Warnakulasuriya et al., 1992). It has been documented that the WHO recommended levels for fluoride in drinking water are not acceptable to all countries and the incidence of dental fluorosis is common even in areas with lower levels of fluoride in water. Therefore, the WHO recommended levels of fluoride in drinking water are not appropriate for many tropical countries and the optimum levels need to be determined considering the climatic conditions, amount of water intake and intake from other sources (WHO, 2011). For instance, drinking of tea, which is one of the common beverages in many regions provide additional fluoride intake (Chandrajith et al., 2007; Fung et al., 1999). In India, dental and skeletal fluorosis have been reported even when the average drinking water fluoride concentration is close to 0.5 mg/L and 0.7 mg/L, respectively, lower than the WHO recommended limits of 1.5 and 4.0 mg/L (Ayoob and Gupta, 2006). Both dental and skeletal fluorosis were more prevalent and more severe in some regions of Senegal where 66.5% of children had mild dental fluorosis at the level of 1.0 mg/L fluoride. Dental fluorosis had reached 100% over 4.0 mg/L of fluoride in drinking water (Brouwer et al., 1988). In Sri Lanka, the optimal level of fluoride in groundwater for caries protection has been recommended to be 0.6-0.9 mg/L (Warnakulasuriya et al., 1992).

GEOCHEMISTRY OF FLUORIDE

Most importantly, the geochemistry of the F-ion (ionic radius 1.36Å) is similar to that of the hydroxyl ion (ionic radius 1.40Å), and therefore, there can be easy exchange between them. When groundwater moves in aquifers, the exchange between fluoride and hydroxyl ions take place leading to the enrichment of fluoride in groundwater. Minerals such as fluorite, apatite, mica, amphiboles are common rock-forming minerals that contain a high amount of fluoride in addition to fluorspar, cryolite, fluoroapatite which have fluoride as a major constituent (Ali et al., 2016). These minerals are abundant in granitic rocks and high-grade metamorphic rocks such as gneisses. Silicate minerals in the earth's crust usually contain fluoride levels as high as 650 mg/kg of fluoride (Adriano, 2001). Prolonged water-rock interactions with a higher rate of mineral weathering which is typical to tropical regions, lead to leaching of fluoride into the solution and in wet climatic regions intense rainfall, washes away fluoride resulting in lower concentrations. On the other hand, the climatic effects, notably evaporation due to the prevailing high ambient temperature can enrich the fluoride concentrations in the water (Dissanayake, 1996; Mukherjee and Singh, 2020). The mobility of fluoride into groundwater is also determined by the groundwater chemistry such as pH, HCO_3^-, and availability of alkali and alkaline earths (Guo et al., 2014; Saxena and Ahmed, 2003). A lowering of Ca-activity with increasing Na/Ca ratios occur due to excessive evaporation of groundwater under tropical conditions and this leads to the increase of fluoride levels (Jacks et al., 2005). However, carbonate rocks act as good sinks for fluoride (Dharmagunawardhane and Dissanayake, 1993) and the leachability of fluoride from the carbonates is controlled by (a) pH of the draining solutions (b) alkalinity (c) dissolved CO_2 and the pCO_2 in the soil. Clay minerals, $Fe(OH)_3$, $Al(OH)_3$ and fine-grained soils adsorb fluoride relatively easily, by displacing hydroxides on the clay surface. Fluoride is effectively adsorbed at a pH range of 3-4 and decreases above 6.5 (Savenko, 2001).

FLUORIDE IN GROUNDWATER OF SRI LANKA

Sri Lanka, a tropical island country with a population of nearly 20 million has well-defined wet and dry zones (Figure 3). In many parts of the island, groundwater is the main source of potable water, particularly in rural communities of the dry zone of Sri Lanka of which over 70 % of communities depend for their domestic needs. The dry zone region comprises almost two thirds of the land area and is characterized by lower rainfall (<1000 mm per annum) with higher evapotranspiration compared to the wet zone which gets over 2500 mm/a rainfall. Restricted rainfall and long dry spells lead to water scarcity in the dry zone regions. In this region, groundwater is mainly extracted from shallow dug wells (<10 m) and deep tube wells. In the dry zone regions, dental fluorosis is highly prevalent, and the exact population affected by dental fluorosis in Sri Lanka is not well known. In some areas in Sri Lanka, dental fluorosis among the population has been recorded as high as 80-98% (Nunn et al., 1994; Warnakulasuriya et al., 1992). Therefore, the hydrogeochemistry of fluoride in drinking water is of major interest.

Geologically Sri Lanka comprises over 90% meta-sedimentary and meta-volcanic rocks of presumed Precambrian age. These rocks are abundant in fluoride-bearing minerals such as micas, hornblende, sphene, and apatite. Further, minerals such as fluorite, tourmaline, and topaz are also found as accessory minerals in many rock types and these also contribute to the general geochemical cycle of fluoride in the geological environment. The fluoride contents of the different types of metamorphic rocks of Sri Lanka varied from 95 mg/kg to 1440 mg/kg (Dharmagunawardhane and Dissanayake, 1993). Groundwater extracted from deep wells in charnockitic gneiss, calc-gneiss, biotite gneiss and on granulite rocks showed higher fluoride contents compared to wells drilled in quartzite and crystalline limestones (Dharmagunawardhane and Dissanayake, 1993). The difference in fluoride levels in aquifer rocks is due to different mineral constituents in these rocks and their relative capability of releasing fluoride ions into groundwater. Deep groundwater is often extracted from fractured crystalline rocks and long residence times enable greater water-rock interaction, which could lead to a higher dissolution of fluoride-bearing minerals. High fluoride regions in Sri Lanka lie within the low plains, whereas the low fluoride zones are mostly confined to the central highlands in the wet zone. High rainfall in the wet zone causes the fluoride to leach out from primary and secondary minerals in rocks and soil whereas, in the dry zone, evaporation tends to bring soluble ions upwards by capillary action. The slow rate of groundwater movement in the low plains also tends to increase the fluoride concentration since the contact time of groundwater with a particular geological formation is comparatively long (Dissanayake, 1996). Even in groundwater extracted from the same aquifer rocks in the dry and wet zones a drastic difference in their fluoride contents has been observed. For instance, some deep wells in the wet zone region showed fluoride contents, often below 0.5 mg/L, indicating a clear influence of climate and hydrology on the fluoride content in groundwater (Dharmagunawardhane and Dissanayake, 1993).

A map showing the distribution of fluoride in groundwater in Sri Lanka had been first compiled in the Hydrogeochemical Atlas of Sri Lanka (Dissanayake and Weerasooriya, 1986) and the fluoride zones of Sri Lanka delineated based on the fluoride content in dug well water samples. It was recently updated with data obtained from many shallow and deep wells (Figure 3) and which showed that a large part of the landmass of Sri Lanka is fluoride-rich (Chandrajith et al., 2012). Over 50% of wells in the dry zone regions have fluoride levels higher than 1.0 mg/L while the fluoride content is also higher in deep wells compared to the shallow wells (Chandrajith et al., 2012). Raghava Rao et al. (1987) noted that high fluoride wells (3-5 mg/L) are mostly associated with charnockites, meta-granites, hornblende biotite gneisses and granitic gneisses whereas moderately fluoride-rich wells (2-3 mg/L) were recognized in garnet-biotite-sillimanite gneisses. In many regions in the North Central Province, the fluoride concentration in groundwater reaches up to 5 mg/L with a high incidence of dental fluorosis. In the very early study of Seneviratne et al. (1974), it had been shown that the prevalence of dental fluorosis in two dry zone districts of Anuradhapura and Polonnaruwa was significant. They showed that 77.5% and 56.2% of the population in these two districts respectively suffer from dental fluorosis in which fluoride levels varied from 0.10-4.70 mg/L and 0.50 to 13.1 mg/L in drinking water. Van Der Hoek et al. (2003) showed that the prevalence of dental fluorosis among 14 year old children were 43.2% in the Udawalawe region where the mean fluoride in groundwater was 0.80 mg/L. Warnakulasuriya et al. (1992) investigated 380 children of about 14 years, living in 4 geographic areas of Sri Lanka with fluoride at 0.09 mg/L to 8.0 mg/L and showed that even in low-fluoride level areas, dental fluorosis is prevalent. A survey carried out in the Aluthwewa village, near Galewela showed that 63% of school children are affected by dental fluorosis, the mean fluoride content of the groundwater being 1.13 mg/L (Ekanayake, 2017).

In recent years, a large number of water quality studies have been carried out particularly in the dry zone regions of Sri Lanka due to the wide attention on CKDu. Fluoride is known to interact with cellular systems including oxidative stress and modulation of intracellular redox homeostasis and some others emphasizing the toxicity of fluoride to human beings even at significantly lower doses (Cittanova et al., 1996). The spatial distribution of CKDu in Sri Lanka mostly overlaps with the regions of high fluoride groundwater and high water hardness (Dissanayake, 2005; Chandrajith et al., 2011a; Chandrajith et al., 2011b). As indicated in recent studies, the fluoride content in dry zone metamorphic terrains varied from 0.02 mg/L to 8.00 mg/L (table 1). The highest mean fluoride content (2.40 mg/L) was recorded in the Madirigiriya area near Polonnaruwa (Jayawardana et al., 2012). However, levels were lower in dry zone sedimentary aquifers systems in the north and north-western part of the island. For instance, the highest mean fluoride content of 0.55 mg/L was recorded in limestone aquifer systems in the Murunkan region (Thilakerathne et al., 2015). Groundwater extracted from sandy aquifers in the dry zone also showed much lower fluoride levels (<0.45 mg/L). In contrast, fluoride levels in wet zone hard rock aquifers are lower than that of the dry zone aquifers.

The other interesting feature of fluoride in groundwater in the hard rock terrain is a drastic variation of the concentrations within short distances. A recent comprehensive investigation carried out using data obtained from 6107 wells indicated that the groundwater fluoride levels in Sri Lanka varied from <0.02 to 12.0 mg/L of which 28% of the wells showed a fluoride level below 0.5 mg/L and 9.7% of wells had over 2.0 mg/L

(Ranasinghe et al., 2019). It was also noted that high fluoride wells (>2 mg/L) were, in some cases located within a distance of 500 m from low fluoride wells (<0.5 mg/L). The minimum distance observed between a high (>2.0 mg/L) and a low fluoride wells (<0.5 mg/L) was 42 m and the maximum distance was 9 km (Ranasinghe et al., 2019). Since low fluoride wells are often located in the vicinity of high fluoride wells, it is very important that the water quality of individual wells be studied for their fluoride contents.

ARSENIC IN GROUNDWATER

Chronic arsenic poisoning caused by drinking water is considered as one of the world's biggest environmental disasters recorded in the last century (Kapaj et al., 2006). Millions of people in Bangladesh and West Bengal were severely affected with arsenic related diseases (Figure 5). The groundwater extracted from clay or peat layers in the Quaternary sediments of the Ganges-Brahmaputra delta consisted of alarmingly high levels of arsenic (Annaduzzaman et al., 2018; Bhattacharya et al., 1997; Bhattacharya et al., 2002). Vietnam, Taiwan, China, Mexico, Nepal, Chile, Myanmar, Cambodia and many parts of the USA and Argentina are among the other countries where high arsenic groundwater had been reported (Ahmed et al., 2004; Rahman et al., 2009). It was reported that over 43 million people in Bangladesh and West Bengal, in India, consume water which has over 10 μg/L As (Chowdhury et al., 2000; Goswami et al., 2020; Rahman et al., 2009). After the outbreak of the chronic arsenic position in Bangladesh, the WHO has lowered the maximum allowable limit of arsenic from 45 μg/L to 10 μg/L. However, up to 3200 μg/L of arsenic had been reported in groundwater in Bangladesh (Bhattacharyya et al., 2003).

Arsenic is a toxic and carcinogenic element present in many rock-forming minerals, mostly associated with iron oxides, clays and in particular sulphide minerals (Bhattacharya et al., 1997). Groundwater obtained from sedimentary aquifers is particularly characterized by higher contents of inorganic As exceeding the WHO recommended values (Ahmed et al., 2004; Bhattacharya et al., 1997; Currell et al., 2011). Once arsenic gets into groundwater, it subsequently enters the human body causing serious health hazards. Skin lesions including skin pigmentation and hyperkeratosis and skin cancer are the most typical symptoms of chronic exposure to arsenic. Lung cancer, blackfoot disease, heart, vascular and kidney diseases are also among other health issues related to the chronic As poisoning (Cohen et al., 2006; Kapaj et al., 2006). However, skin diseases are the most common health effects of chronic As poisoning that was reported in people who consume drinking water even with 5 μg/L of As (Yoshida et al., 2004).

Since arsenic is a metalloid, naturally occurring arsenic occurs in groundwater as oxy-anions of As(III) or As(V). Compared to organic forms of arsenic such as As-betaine, mono-methyl or dimethyl arsenate, inorganic arsenic is considered to be more toxic (Sharma and Sohn, 2009; Smedley and Kinniburgh, 2013). However, organic forms of arsenic are mostly found in food and from among the inorganic forms, the more toxic form As(III), enters the body mainly through drinking water. Even As(V) reduces to As(III) after entering the cell membranes (Jomova et al., 2011).

ARSENIC IN GROUNDWATER IN SRI LANKA

Recent hydrogeochemical investigations indicated that alarmingly high arsenic-containing groundwater is not present in the high-grade metamorphic terrains of Sri Lanka (Nanayakkara et al., 2019; Wickramarathna et al., 2017). In particular, groundwater in this terrain is extracted from the weathered overburden or tensional fractures in the metamorphic rocks. In recent years, arsenic in groundwater received wider attention as it was proposed as an etiological factor for the occurrence of CKDu in Sri Lanka (Jayasumana et al., 2015; Jayatilake et al., 2013).

Despite public debates on high arsenic in drinking water and its relationship with the CKDu, alarmingly higher concentrations of arsenic in water and soil have not been reported in the geological materials in Sri Lanka. High grade metamorphic rocks of Sri Lanka contain exclusively low arsenic contents. Chandrajith et al. (2001) investigated several types of high-grade metamorphic rock such as gneisses, charnockites, granulites, which contained less than 5 mg/kg of arsenic, indicating the non-availability of arsenic-bearing minerals. Soils are other natural materials that can easily be contaminated with arsenic due to the application of fertilizer and pesticides. Jayawardana et al. (2014) reported that agricultural soils contain relatively higher contents of arsenic (1.0-24 mg/kg) compared to non-agricultural soils (1.0-4.0 mg/kg). However, organic rich, uncontaminated forest soils collected from the Udawalawe region in the dry zone had 9-29 mg/kg As (Chandrajith et al., 2009). A study of 70 paddy soils, collected from different terrains of Sri Lanka contained only 0.85 mg/kg of arsenic as the mean, while soils from both dry and wet zones showed almost similar As levels (Chandrajith et al., 2005). Soils collected from two CKDu affected regions (Medawachchiya and Medirigiriya) in the dry zone of Sri Lanka showed 3.39- 11.9 mg/kg of arsenic with a mean value of 7.32 mg/kg (Levine et al., 2016). Sediments from a dry zone reservoir showed an arsenic content of 0.5 to 24 mg/kg (mean 8.3 mg/Kg) (Chandrajith et al., 2008). Although phosphate fertilizer is claimed to be a source of inorganic arsenic in cultivated soils (Jayasumana et al., 2015), the reported soil As levels were relatively low and negligible.

Inorganic arsenic in groundwater is mostly leached from the aquifer rocks, but anthropogenic activities such as an application of phosphate fertilizer can also add arsenic into groundwater. The leaching of arsenic from aquifer materials depends on the geochemical characteristics of groundwater. The most common mechanism for the release of arsenic is dissolution under reducing conditions (Anawar et al., 2004; Bhattacharya et al., 1997; Tufano and Fendorf, 2008). Higher organic contents in aquifers could enhance the release of As into groundwater (Redman et al., 2002; Wang and Mulligan, 2006). Alkaline conditions in groundwater also favour the release of arsenic from aquifer materials (Fendorf and Kocar, 2009). Oxidation of sulfide minerals such as arsenopyrite (FeAsS), and arsenian pyrite [$Fe(SAs)_2$] also can release arsenic into groundwater (Smedley, 2008).

Although arsenic-contaminated groundwater is not reported particularly in metamorphic aquifers, elevated levels were reported in certain parts of the island (table 2). It has been reported that groundwater from Mannar (Figure 5), Mulativu, Puttalam, and Jaffna (Figure 6) has high arsenic levels compared to other parts of the island (Amarathunga et al., 2019; Bandara et al., 2018; Herath et al., 2018). In all these regions, groundwater is extracted from unconfined aquifers in the Holocene sand dunes that are underlain by Miocene limestones. For instance, over 30% of the shallow wells in the Mannar island exceeded the WHO recommended limits of arsenic (Bandara et al., 2018)(Figure 4). Groundwater in the wet zone region of Sri Lanka has extremely low levels of arsenic, sometimes less than 0.01 μg/L. In the dry zone regions where CKDu is widespread, arsenic levels are lower than the recommended values of the WHO.

REMOVAL OF FLUORIDE AND ARSENIC FROM DRINKING WATER

Since there are no beneficial roles of high fluoride and arsenic, reduction of these parameters from drinking water is most important. The problem of high fluoride and arsenic in drinking water can be observed mostly in rural regions of Sri Lanka. In such regions, centralized water supply networks are unavailable and a majority of the population depends on groundwater. Due to a low socio-economic background, rural communities cannot offer expensive household level or community based water purification systems. Therefore, developing a cheap, simple and easily to use, household level water filtration system is necessary for the mitigation of the fluoride and arsenic problems. Although the arsenic problem is only restricted to small regions, high fluoride groundwater is a widespread problem in many dry zone regions of Sri Lanka. The consumers are unaware of the presence of excess fluoride or arsenic since both parameters do not affect the taste, colour or the smell of water.

Many techniques had been introduced for fluoride removal and most methods are based on the affinity of fluoride towards hydroxyl group or tendency of adsorbing ferrous and aluminium ions. Among these techniques, adsorption processes are used widely and in most cases natural geological materials were used as adsorbing agents (Bhatnagar et al., 2011). In Sri Lanka, several studies had been carried out to introduce village level or household level defluoridation methods that can remove fluoride into the safe limits. From among these techniques, use of locally available brick and tile chips, kaolinite clay, laterite, apatite and sepentinite showed promising results (Jinadasa et al., 1991; Nikagolla et al., 2013; Padmasiri and Dissanayake, 1995; Weerasooriya et al., 1998). These materials are widely available in Sri Lanka and can be used for developing household level defluoridators. Removal of arsenic from contaminated drinking water is also widely studied and coagulation, ion exchange and adsorption on to aluminium or iron oxides were the technique used for arsenic removal. Naturally occurring red sand in north and northwestern coastal area were used effectively to remove both arsenate and arsenite (Vithanage et al., 2014). Their studies showed that almost all arsenic species can be removed from contaminated in pH range of 4-8.

CONCLUSIONS

This review has attempted to investigate the fluoride and arsenic geochemistry in the groundwater of Sri Lanka. As shown in previous studies, excessive fluoride-containing groundwater is a major problem in the dry areas of Sri Lanka. In this region, a large population suffers from chronic fluoride poisoning, in view of the fact that over 80% of the population uses groundwater for drinking purposes. This leads to the condition of dental fluorosis and in some cases to skeletal fluorosis until the later stages of symptoms appear. Although, geologically, both dry and wet zones of Sri Lanka do not show major differences, groundwater fluoride levels are drastically different. This clearly indicates that under semi-arid conditions, fluoride tends to increase in groundwater due to low precipitation and high evaporation. Since high fluoride lead to severe health hazards, introducing household level defluoridation techniques are urgently required in high fluoride regions. Identification of low fluoride wells in village level also helps to provide drinking water for the rural communities, since low fluoride wells are sometimes located in the close vicinity of high fluoride wells. Since communities in the dry zone of Sri Lanka ingest excessive levels of fluoride through drinking water and also through regular consumption of black tea with high fluoride, estimation of the daily intake and associated health hazards need to be assessed. Arsenic is not observed as a critical issue in the island, particularly in the metamorphic terrain. Excessive levels, however, were recorded in sedimentary aquifers. It is obvious that local geological conditions are responsible for the higher contents arsenic in the groundwater of Sri Lanka.

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Figure Captions

Figure 1: Regions with fluoride concentration in the groundwater exceeding WHO guidelines for drinking water of 1.5 mg/L.

Figure 2: A typical case of dental fluorosis in the dry zone of Sri Lanka

Figure 3: Climatic boundaries and provinces (1- Western; 2-Sabaragamuwa; 3-Sothern; 4-Central; 5-Uva; 6-Wayamba; 7-North Central; 8- Eastern and 9- Northern) of Sri Lanka.

Figure 4: Distribution of fluoride in Sri Lanka (after Chandrajith et al., 2012).

Figure 5: Arsenic distribution in Mannar Island, Sri Lanka.

Figure 6: Arsenic distribution in Jaffna Peninsula, Sri Lanka.

Table Captions

Table 1: Fluoride (mg/L) contents reported in different regions of Sri Lanka (N-number of samples; LS- Limestone; SD- Sandy aquifers). Details of locations are shown in Figure 3.

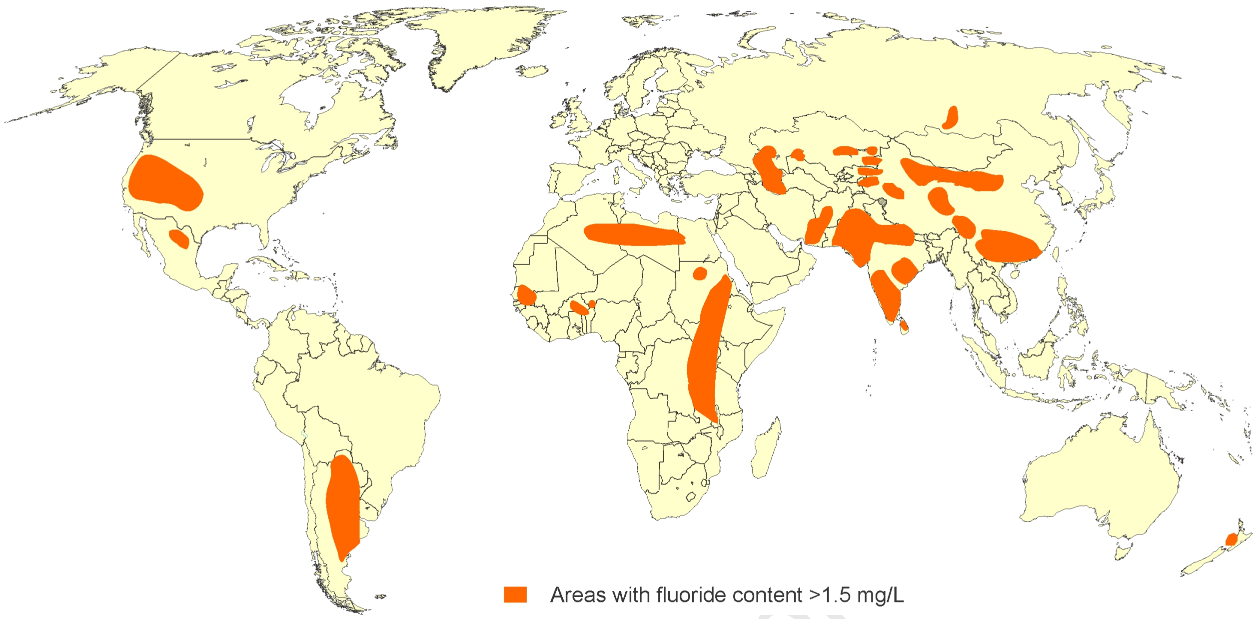
Table 2: Arsenic (µg/L) content in groundwater from different regions of Sri Lanka. Location details are shown in figure 3 (N-number of samples; LS- Limestone).

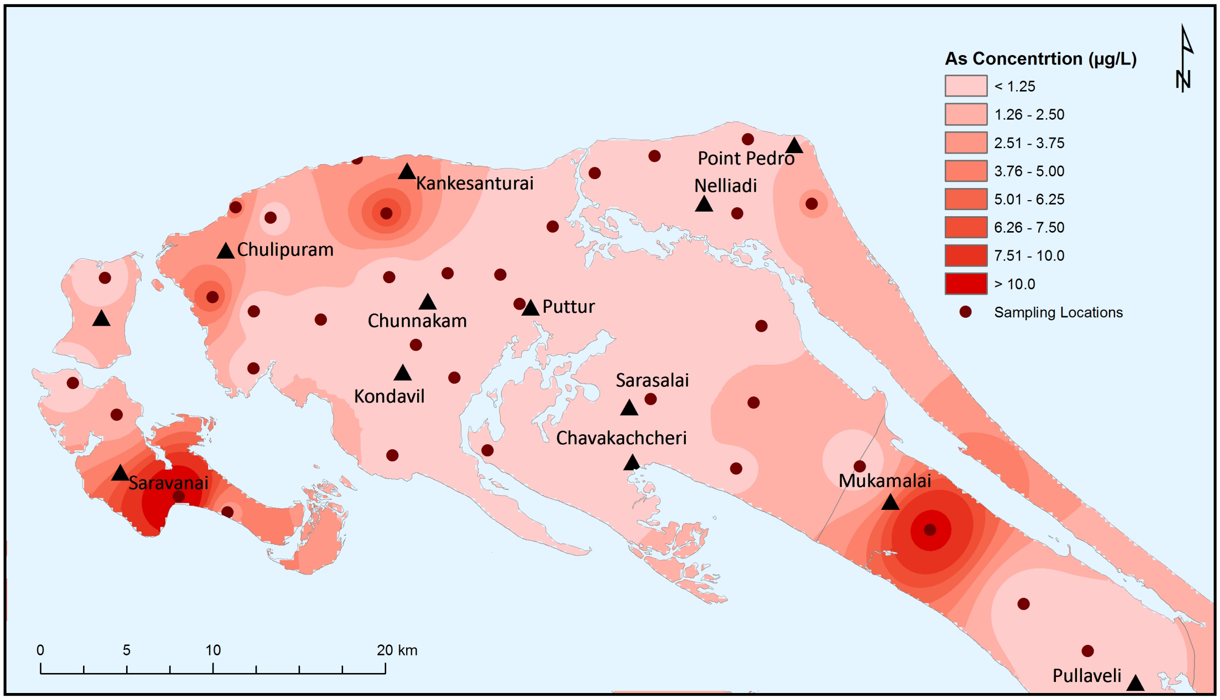
Table 1: Fluoride (mg/L) contents reported in different regions of Sri Lanka (N-number of samples; LS- Limestone; SD- Sandy aquifers). Details of locations are shown in Figure 3.

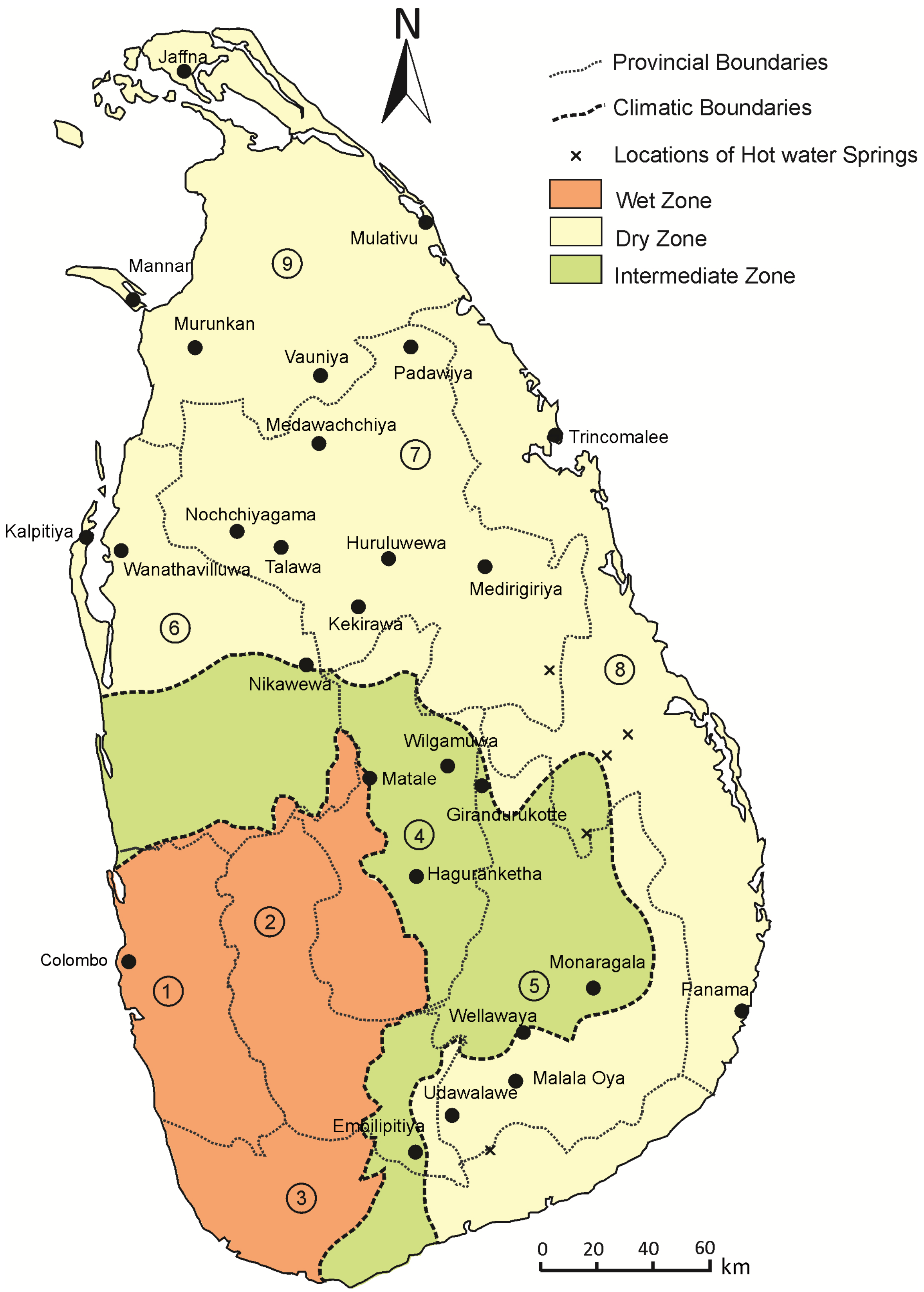
Region	N	Mean F	Range	Reference
Dry Zone-Metamorphic aquifers				
Galewela	44	1.02	0.04-5.00	Ekanayake (2017)
Girandurukotte	46	0.64	0.02-2.14	Chandrajith et al. (2011b)
Girandurukotte	52	0.76	0.02-2.50	Wickramarathna et al. (2017)
Giribawa-Nochchiyagama	170	0.90	<0.02-4.34	Young et al. (2011)
Huruluwewa	29	0.72	0.02-1.68	Chandrajith et al. (2011a)
Kakirawa	124	0.57	0.04-3.16	Young et al. (2011)
Madirigiriya		2.40	0.20-8.00	Jayawardana et al. (2012)
Malala Oya basin	30	1.51	0.12-3.42	Senarathne et al. (2019)
Malala Oya basin (surface water)	7	0.54	0.10-1.15	Senarathne et al. (2019)
Medawachchiya	10	1.42	0.52-4.90	Chandrajith et al. (2011a)
Medawachchiya/Maderigiriya	91	0.60	0.07-1.05	Levine et al. (2016)
Monaragala	111	0.89	0.02-2.93	unpublished data
Murunkan	8	0.41	0.02-0.72	Thilakerathne et al. (2015)
Nikawewa	52	1.21	0.02-5.30	Chandrajith et al. (2011a)
Nikawewa	7	1.61	0.43-3.44	Wickramarathna et al. (2017)
Padaviya	34	0.62	0.02-1.33	Chandrajith et al. (2011a)
Padaviya	-	0.40	0.20-1.00	Jayawardana et al. (2012)
Talawa	-	1.70	0.20-4.00	Jayawardana et al. (2012)
Udawalawe (Shallow wells)	416	0.57	0.04-3.16	Van Der Hoek et al. (2003)
Udawalawe (deep wells)	63	0.80	0.18-5.20	Van Der Hoek et al. (2003)
Udawalawe (surfac water)	27	0.22	0.20-0.87	Van Der Hoek et al. (2003)
Wilgamuwa	12	1.04	0.15-5.47	Wickramarathna et al. (2017)
Wellawaya	8	1.05	0.45-2.20	Chandrajith et al. (2011a)
Dry Zone-Sedimentary aquifers				
Mannar (LS)	35	0.41	0.02-1.90	Bandara et al. (2018)
Wanathawilluwa basin (LS)	28	0.53	0.06-1.49	Unpublished data
Jaffna (LS)	35	0.38	0.08-1.54	Chandrajith et al. (2016)
Murunkan (LS)	21	0.55	0.02-0.84	Thilakerathne et al. (2015)
Kalpitiya Peninsular (SD)	43	0.45	0.02-1.57	Unpublished data
Panama (SD)	30	0.44	<0.02-1.30	Chandrajith et al. (2014)
Wet Zone-Metamorphic aquifers				
Matale	23	0.19	0.10-0.52	Chandrajith et al. (2015)
Haguranketha	83	0.25	0.05-0.74	Abeywickarama et al. (2016)
Kandy	30	0.05	0.02-0.06	Wasana et al. (2016)
Nuwara Eliya	30	0.06	0.03-0.10	Wasana et al. (2016)
Gampaha	30	0.02	0.01-0.47	Wasana et al. (2016)
Others				
Hot water Springs	7	3.50	0.12-5.95	Chandrajith et al. (2013)

Table 2: Arsenic (µg/L) in groundwater from different regions of Sri Lanka. Details of locations are shown in figure 3 (N-number of samples; LS- Limestone).

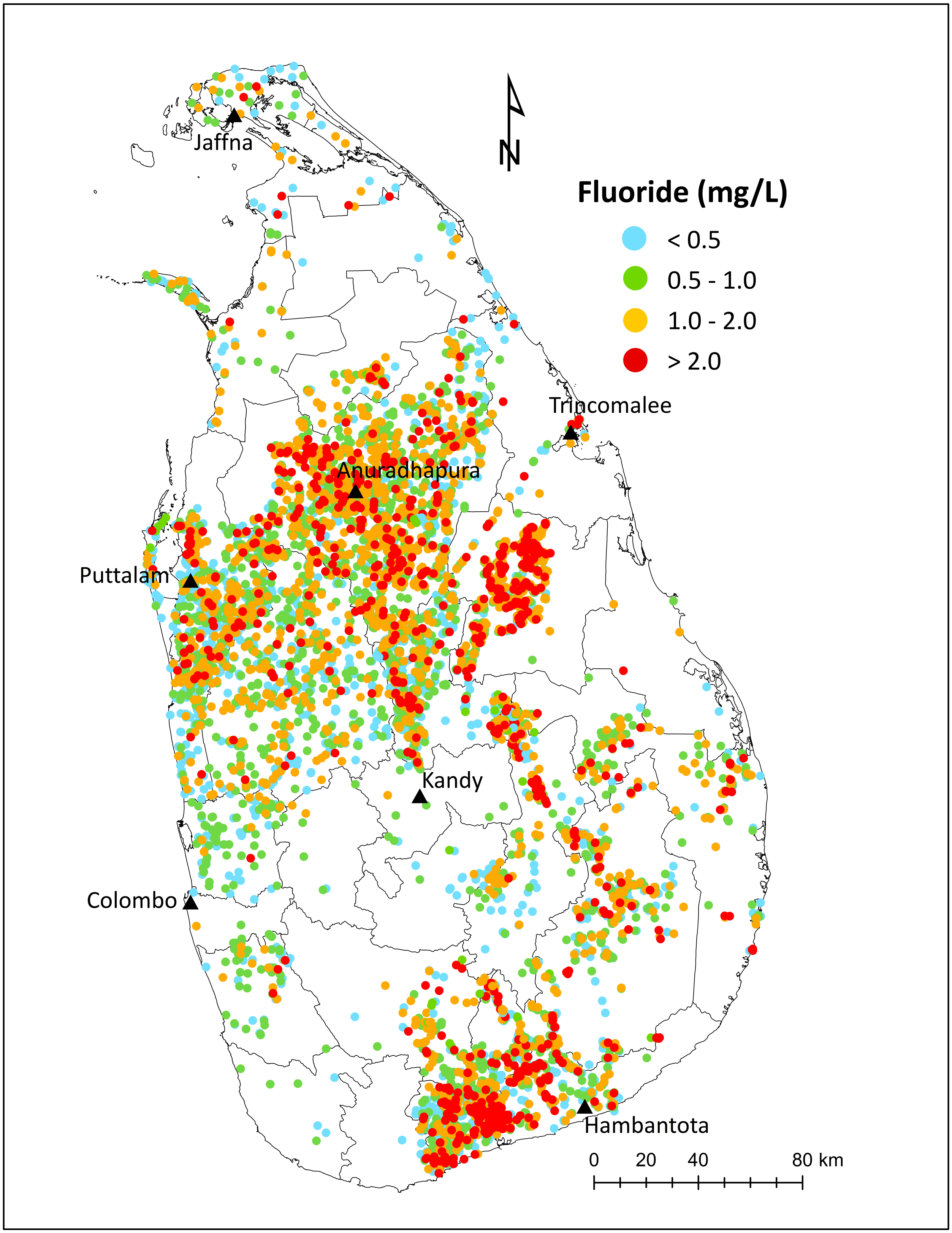
Region	N	Mean As	Range	Reference
Dry Zone-Metamorphic aquifers				
Girandurukotte	29	0.26	0.06-1.90	Nanayakkara et al. (2019)
Malala Oya basin	30	0.25	0.07-0.65	Senarathne et al., (2019)
Girandurukotte	52	0.23	<0.15-0.73	Wickramarathna et al. (2017)
Wilgamuwa	12	0.36	<0.15-1.64	Wickramarathna et al. (2017)
Nikawewa	7	0.19	<0.15-0.51	Wickramarathna et al. (2017)
Dry Zone-Sedimentary aquifers				
Mannar Island (LS)	-	7.0	66 (max)	Herath et al. (2017)
Mannar Island (LS)	35	8.38	0.60-34.0	Bandara et al. (2018)
Tharapuram-Mannar (LS)	8	25.5	6.5-43.8	Amarathunga et al. (2019)
Jaffna (LS)	35	2.0	0.10-15.1	Chandrajith et al. (2016)
Mulative	-	3.0	13 (max)	Herath et al. (2017)
Puttalama	-	4.0	15 (max)	Herath et al. (2017)

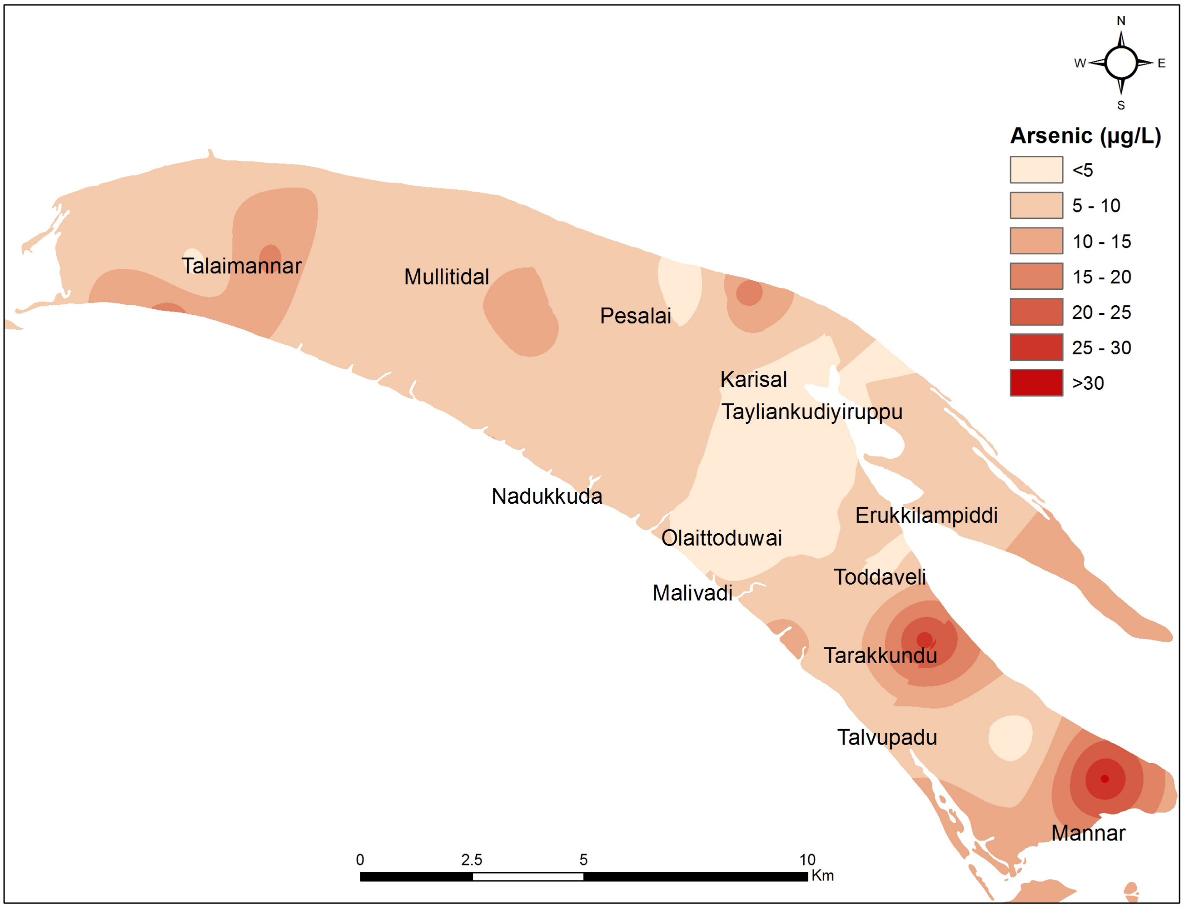

Areas with fluoride content >1.5 mg/L


As Concentrtion (μg/L)
< 1.25
1.26 - 2.50
2.51 - 3.75
3.76 - 5.00
5.01 - 6.25
6.26 - 7.50
7.51 - 10.0
> 10.0
Sampling Locations
N
Kankesanturai
Chulipuram
Chunnakam
Puttur
Kondavil
Point Pedro
Nelliadi
Sarasalai
Chavakachcheri
Saravanai
Mukamalai
Pullaveli
0
5
10
20 km



N
Provincial Boundaries
Climatic Boundaries
Locations of Hot water Springs
Wet Zone
Dry Zone
Intermediate Zone
Jaffna
Mulativu
Mannar
Murunkan
Vauniya
Padawiya
Medawachchiya
Trincomalee
Kalpitiya
Nochchiyagama
Huruluwewa
Wanathavilluwa
Talawa
Medirigiriya
Kekirawa
Nikawewa
Wilgamuwa
Matale
Girandurukotte
Haguranketha
Colombo
Monaragala
Panama
Wellawaya
Malala Oya
Udawalawe
Embilipitiya
1
2
3
4
5
6
7
8
9
0
20
40
60
km


Fluoride (mg/L)
< 0.5
0.5 - 1.0
1.0 - 2.0
> 2.0
N
Jaffna
Trincomalee
Anuradhapura
Puttalam
Kandy
Colombo
Hambantota
0
20
40
80 km


N
W
E
S
Arsenic (µg/L)
<5
5 - 10
10 - 15
15 - 20
20 - 25
25 - 30
>30
Talaimannar
Mullitidal
Pesalai
Karisal
Tayliankudiyiruppu
Nadukkuda
Erukkilampiddi
Olaittoduwai
Toddaveli
Malivadi
Tarakkundu
Talvupadu
Mannar
0
2.5
5
10
Km

Highlights

- Fluoride and arsenic dissipation in the groundwater in Sri Lanka is reviewed.
- Groundwater in dry regions show elevated fluoride levels causing dental and skeletal fluorosis
- Introducing a household level defluoridating method is required for the high fluoride regions.
- Naturally occurring groundwater with high As (>10µg/L) is recorded in sedimentary aquifers.

CONFLICT OF INTEREST STATEMENT

On behalf of all authors whose names given below, I hereby certify that, to the best of my knowledge:

This manuscript has not been published and is not under consideration for publication elsewhere. All authors have participated in conception and design, or analysis and interpretation of the data; drafting the article and approval of the final version. Authors declare that there is no conflict of interest.

All persons who meet authorship criteria are listed as authors, and all authors certify that they have participated sufficiently in the work to take public responsibility for the content, including participation in the concept, design, analysis, writing, or revision of the manuscript. Furthermore, each author certifies that this material or similar material has not been and will not be submitted to or published in any other publication.

All persons who have made substantial contributions to the work reported in the manuscript (e.g., technical help, writing and editing assistance, general support), but who do not meet the criteria for authorship, are named in the Acknowledgments and have given us their written permission to be named. If we have not included an Acknowledgments in our manuscript, then that indicates that we have not received substantial contributions from non-authors.

The authors whose names are listed immediately below certify that they have NO affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

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