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Co-occurrence of arsenic and fluoride in groundwater of semi-arid regions in Latin America: Genesis, mobility and remediation

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HIGHLIGHTS

- As and F co-occurrence in groundwater is linked to volcanism, geothermal, and mining activities.
- As and F co-occurrence are particularly pronounced in arid and semi-arid regions.
- As and F are generally associated to high concentrations of Na^+ and HCO_3^-.
- Technology is required to simultaneously remove As and F from drinking water.

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ABSTRACT

Several million people around the world are currently exposed to excessive amounts of arsenic (As) and fluoride (F) in their drinking water. Although the individual toxic effects of As and F have been analyzed, there are few studies addressing their co-occurrences and water treatment options. Several studies conducted in arid and semi-arid regions of Latin America show that the co-occurrences of As and F in drinking water are linked to the volcaniclastic particles in the loess or alluvium, alkaline pH, and limited recharge. The As and F contamination results from water–rock interactions and may be accelerated by geothermal and mining activities, as well as by aquifer over-exploitation. These types of contamination are particularly pronounced in arid and semi-arid regions, where high As concentrations often show a direct relationship with high F concentrations. Enrichment of F is generally related to fluorite dissolution and it is also associated with high Cl, Br, and V concentrations. The methods of As and F removal, such as chemical precipitation followed by filtration and reverse osmosis, are currently being used at different scales and scenarios in Latin America. Although such technologies are available in Latin America, it is still urgent to develop technologies and methods capable of monitoring and removing both of these contaminants simultaneously from drinking water, with a particular focus towards small-scale rural operations.

1. Introduction

The occurrence of As and F in groundwater has been widely reported in Latin America, especially in arid and semi-arid regions of Mexico, Argentina, and Chile. Unfortunately, it is often the case that F is not considered to be a problem, reason for which its presence has not even been determined in many places of Latin America. Due to its high toxicity, As removal techniques have been a major research focus during the last two decades [1]. Interestingly, a geological co-occurrence of these contaminants has been reported by numerous investigators from El Salvador, Peru, Bolivia, Nicaragua, Ecuador, Colombia, and Guatemala [2–4]. There is a high probability that F might occur in other Latin American regions, especially in places with arid and semi-arid conditions, where As in drinking

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water has been detected and where the aquifer has been characterized by a mixture of calcareous and volcanoclastic sediments, rocks such as shale and sandstone, or alkaline groundwaters of $Na–HCO_3^-$ type [5]. Although this study focuses in Latin America, the problem of high F and As concentrations is far reaching. Areas that are not monitoring F may find that it is present in high concentrations, and new developments in arid areas may strain the availability of groundwater, drawing water from deeper parts of the aquifer where these contaminants can be in greater concentrations. In addition, arid areas with reported co-occurrence of As and F in countries other than Latin America may face similar shortages in economic resources, considering that in developing countries the groundwater resources are prone to contamination [6,7]. In the last section of this paper, the analysis and discussion on treatments for water contaminated with As and F apply to all arid areas of limited economic resources, and are not restricted to Latin America.

In many Latin American regions, the dissolved As and F concentrations show a significant co-occurrence [7–9], thus enhancing the health risks posed by HACRE (Spanish acronym for Hidroarsenicismo Crónico Regional Endémico – Endemic Regional Chronic Hydroarsenicism) [10] and/or fluorosis, either dental or skeletal [11]. Millions of people in Latin America could be currently exposed to As and F through drinking water [9–14]. In Mexico alone, approximately 6 million people are exposed to both pollutants [15–17]. Little is known about the toxic effects stemming from a co-exposure to As and F [6,17], but they could lead to both HACRE and endemic fluorosis. The exposure to either As or F has shown to induce reduced IQ levels and decreased intellectual functionality amongst children [18–20]. Recent studies explored the effect of exposure to both pollutants on immune cells in human populations with chronic exposure through drinking water [20–22]. The presence of As and F could be seen by comparing gene expression profiles in humans exposed to both contaminants with the profiles from populations exposed to these elements individually. The interaction of As with other elements could be a key in the complete elucidation of the molecular mechanisms involved in the development of inflammatory and malignant diseases [21,22].

The solution to the problem of drinking water with As and F requires either tapping alternative water sources or contaminated water treatment. Several conventional processes for the removal of the individual contaminants exist, but only a few can simultaneously remove both contaminants [1,2,23]. Many of these methods are a combination of conventional and advanced technologies, which are mainly used to treat As concentrations in urban groundwater supplies. Once again, the removal of F has not been considered as important as that of As, even though it can co-occur with As in most of the semi-arid regions of Latin America.

This manuscript presents a short overview of the co-occurrence of As and F in drinking water sources by means of some key studies conducted in the Latin American countries of Mexico, Argentina, and Chile. Although the results have been partially and independently reported elsewhere, the authors aim to show a greater picture of the factors that affect the occurrence of As and F, emphasizing the similarities and differences between the studied areas. Along with their co-occurrence, this study also discusses the genesis and mobility of these contaminants, addresses the treatments being utilized for the removal of As and F in some of the affected areas of Latin America.

2. Co-occurrence of arsenic and fluoride in groundwater

2.1. Mexico

In Mexico, ~75% of the total population relies on groundwater for drinking. Some communities have been diagnosed with HACRE and hydrofluorosis, especially in arid and semi-arid regions of central and northeastern Mexico [3,4,8,15,24,25]. The presence of As in these areas has been reported over the past decade, while F determinations have only been recently performed. Many areas contain As and F levels above the Mexican drinking water standards of 0.25 and 1.5 mg/L, respectively [24–31].

The predominant geology of the arid and semi-arid areas analyzed in this work is characterized by the outcrops of Paleozoic and Mesozoic sedimentary rocks, Tertiary igneous rocks, and marsh and lake deposits. Along the coast of Sonora, aquifers are comprised of sedimentary rocks of marine origin. The windblown deposits from the Quaternary period formed the filled valleys with conglomerates and alluvial soils [32–35]. The igneous material, together with the conglomerates and the Quaternary alluvium derived from it, is believed to be the source of As and F in several aquifers in the States of Chihuahua, Sonora, Durango, and San Luis Potosí [36,37]. The aforementioned geological compositions, together with conditions of aridity, generate greater concentrations of As and F that are intensified by the high evaporation, rain shortage, and fluctuation of water levels that result from excessive water extraction [38].

Arid and/or semi-arid climates dominate from northern Mexico to the central states of San Luis Potosi, Jalisco, and Michoacán; whose annual rainfall varies between 200 mm in the northern region and 900 mm in the central part [39].

This study identified three main hydrogeological environments that contain high As and F concentrations: areas of geothermal activity (central and northern Mexico), alluvial aquifers (northern Mexico), and areas of mining activity (north-central Mexico).

2.1.1. Areas of geothermal activity

Most of the high As and F concentrations occur where there is upwelling of water characteristic of geothermal and volcanic areas in closed basins. This water upwelling indicates a possible correlation between As and F due to the water quality conditions that favor the migration of both elements [40].

Los Azufres, Michoacán (Fig. 1, location 13), shows a natural contamination of geothermal As and F (5.1–24 mg/L and 9–17 mg/L, respectively). In addition to this, the concentrations in Los Azufres have increased since 1982, after the establishment of a power plant that uses evaporation ponds and sometimes re-injects wastewater into the aquifer. A two-year study showed the increased levels of As (from 2 to 32 mg/L) and F (10–90 mg/L) in the groundwater from Los Azufres [41]. Although this water is intended for industrial use and has different conditions, it shows how evaporation results in increased As and F concentrations; which can be extrapolated to explain the evaporation occurring in arid areas.

Las Tres Vírgenes (Fig. 1, location 1) is also found under an arid climate and encompasses an alluvial aquifer that lies above a granular basement [32,33]. The concentration of As in Las Tres Vírgenes is relatively constant (6.5–6.7 mg/L) and its probable origin has been reported as a dissolution of primary minerals followed by a dispersion of As [41]. In both Los Azufres and Las Tres Vírgenes geothermal reservoirs, data shows relatively constant As concentrations throughout varying temperature conditions; these temperatures range between 230 and 250 °C, providing optimal and stable conditions for As mobility [41].

The Araró hot springs region is located in the northern part of Michoacán (Fig. 1, location 12). This region has a moderate to semi-arid climate, with an average annual precipitation of 906 mm. The site was included here because of the high As and F found in its waters, which is due in part to geothermal activity [33,34]. Arsenic concentrations varied from 0.01 to 63 mg/L, and F concentrations range from 0.7 to 4.2 mg/L. The highest As and F concentrations were found at sites where water temperature was close to its