Science of the Total Environment 593–594 (2017) 211–226

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Characterization of regional cold-hydrothermal inflows enriched in arsenic and associated trace-elements in the southern part of the Duero Basin (Spain), by multivariate statistical analysis

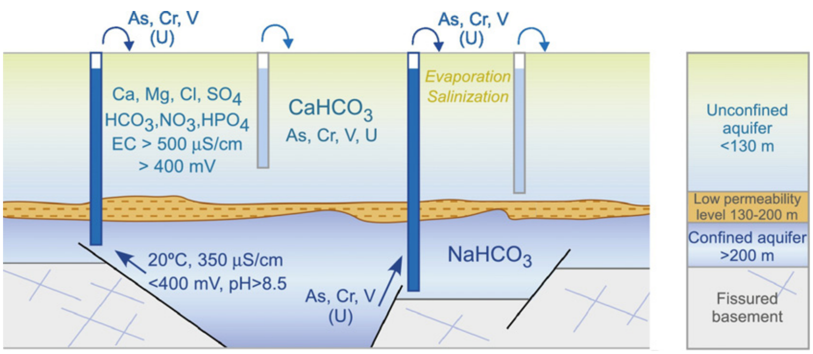
Elena Giménez-Forcada [a,*], Marisol Vega-Alegre [b], Susana Timón-Sánchez [a]

[a] Instituto Geológico y Minero de España—IGME, Unidad de Salamanca, Azafranal 48, 37001 Salamanca, Spain
[b] University of Valladolid—UVA, Department of Analytical Chemistry, Campus Miguel Delibes, Paseo Belén 7, 47011 Valladolid, Spain

HIGHLIGHTS

- High-As groundwaters are identified in the contact area of the Duero Basin-Spanish Central System.
- Structural control of As distribution in groundwaters of this area is marked.
- Cold-hydrothermal $NaHCO_3$ waters linked to the deep confined aquifer were identified.
- Alkaline $NaHCO_3$ waters are recognized as the primary source of As, V, Cr, (and U).

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 October 2016
Received in revised form 7 March 2017
Accepted 8 March 2017
Available online 24 March 2017

Editor: D. Barcelo

Keywords:
Arsenic
Chromium
Uranium
Vanadium
Hydrochemistry
Multivariate statistical analysis

ABSTRACT

Naturally occurring arsenic in groundwater exceeding the limit for potability has been reported along the southern edge of the Cenozoic Duero Basin (CDB) near its contact with the Spanish Central System (SCS). In this area, spatial variability of arsenic is high, peaking at 241 μg/L. Forty-seven percent of samples collected contained arsenic above the maximum allowable concentration for drinking water (10 μg/L).

Correlations of As with other hydrochemical variables were investigated using multivariate statistical analysis (Hierarchical Cluster Analysis, HCA and Principal Component Analysis, PCA). It was found that As, V, Cr and pH are closely related and that there were also close correlations with temperature and Na^+. The highest concentrations of arsenic and other associated Potentially Toxic Geogenic Trace Elements (PTGTE) are linked to alkaline $NaHCO_3$ waters ($pH \approx 9$), moderate oxic conditions and temperatures of around 18 °C–19 °C. The most plausible hypothesis to explain the high arsenic concentrations is the contribution of deeper regional flows with a significant hydrothermal component (cold-hydrothermal waters), flowing through faults in the basement rock. Water mixing and water-rock interactions occur both in the fissured aquifer media (igneous and metasedimentary bedrock) and in the sedimentary environment of the CDB, where agricultural pollution phenomena are also active. A combination of multivariate statistical tools and hydrochemical analysis enabled the distribution pattern of dissolved As and other PTGTE in groundwaters in the study area to be interpreted, and their most likely origin to be established. This methodology could be applied to other sedimentary areas with similar characteristics and problems.

---

* Corresponding author.
E-mail address: e.gimenez@igme.es (E. Giménez-Forcada).

http://dx.doi.org/10.1016/j.scitotenv.2017.03.071
0048-9697/

1. Introduction

Arsenic is a ubiquitous element widely distributed in the environment and highly toxic in its inorganic form. High levels of inorganic arsenic are naturally present in groundwater in a number of countries, including Argentina, Chile, China, Mexico, Bangladesh, India and the United States, and it poses a problem in a growing number of areas and many new cases are likely to be discovered (WHO, 2016; Smedley and Kinniburgh, 2002; Thakur et al., 2011; Kumar et al., 2016). Long-term exposure to inorganic arsenic due to drinking of contaminated water and eating of food prepared with this water can lead to chronic arsenic poisoning (WHO, 2016).

Most high-As groundwaters are the result of natural occurrences of As and this is common to a wide range of environments. These natural conditions include both oxidizing (under conditions of high pH) and reducing aquifers, as well as areas affected by geothermal activity. Moreover, evaporation needs to be taken into account because this process can increase concentrations substantially (Smedley and Kinniburgh, 2002). These statements concern natural As and exclude anthropogenic sources of As from mining, and industrial and agricultural pollution (from arsenical pesticides).

However, high concentrations of As in groundwaters are not necessarily related to aquifer rock matrices containing high As concentrations (Smedley and Kinniburgh, 2002). According to Stüben et al. (2003), the mechanism of As solubilization can be more important than the type or size of the source, and sometimes high-As groundwaters occur in areas where only moderate levels of arsenic occur in the host rock (Garelick et al., 2008). For this reason, where high As concentrations occur, it is important to analyze not only all the potential sources, but also the factors or conditions controlling its geographical distribution.

A common characteristic of aquifers affected by high levels of As is the spatial variability in As concentration in the groundwater (e.g. Smedley and Kinniburgh, 2002; Eiche, 2009). Nearby sampling points may yield very different concentrations, making it very difficult to predict concentrations in a particular area based on results from the surrounding area.

In Cenozoic sedimentary areas of central Spain associated with the Spanish Central System (SCS), such as the Tagus Basin (TB) and the Cenozoic Duero Basin (CDB) (Fig. 1a), problems have arisen when naturally occurring arsenic and other Potentially Toxic Geogenic Trace Elements (PTGTEs) (e.g. V, U) exceed the limit concentrations for potability (e.g. Hernández-García and Custodio, 2004; Gómez et al., 2006). One of the most seriously affected areas is the southern edge of the CDB (e.g. Sahún et al., 2003), along its contact with the Spanish Central System (SCS). Here, concentrations of As are often only slightly above the allowable maximum concentration (10 μg/L, WHO, 2011), but this is sufficient to invalidate its use as drinking water. For this reason, significant volumes of groundwater are rejected as a supply source as being unfit for consumption. Groundwater is a vital resource in this semi-arid region, where it is used mainly for public supply and agriculture. The scarcity of surface water resources has led to an intense—and sometimes uncontrolled—exploitation of groundwater in recent decades.

Investigations to date in the south of the CDB concur in attributing the presence of arsenic to water-sediment reactions under particular pH and redox conditions (e.g. García-Sánchez et al., 2005; Gómez et al., 2006; Pardo et al., 2008). These associate the mobilization of this metalloid with desorption of the oxyhydroxides of Fe and Mn in the sediment, under oxic conditions and alkaline pH (e.g. Smedley and Kinniburgh, 2002; Telfeyan et al., 2015). Analysis of sediment samples in the CDB undertaken by Pardo et al. (2008), Delgado et al. (2009) and Carretero (2016) reveal that the clayey-silty deposits contain the highest levels of As, making them potential sources of arsenic to groundwater in contact with this kind of sediment.

Although the studies undertaken until now have made a significant contribution to knowledge of this issue, certain questions remain, such as identifying the primary sources of As and associated trace elements, the processes going on in the catchment and the reasons for its apparently patchy geographical distribution. From a broader perspective, an attempt by Giménez-Forcada and Smedley (2014) to identify the origin of As and the reasons for its spatial heterogeneity in the southern CDB, established that As distribution is strongly determined by the basin's structure and the morphology of its basement. A detailed discussion of the geochemical environment that characterizes groundwaters and the influence of basement structure in the control of As distribution pattern is given in this cited study. The authors identified that the highest concentrations of As are associated with the prolongation of significant faults of SCS in the CBD (e.g. Muñico Fault and Messejana Plasencia dyke, MPD, Fig. 1), and that point hydrothermal mineral deposits of the SCS are the primary sources of As. They also highlight the effect of alkaline pH on the desorption of arsenates from CBD sediments, under oxidizing conditions. This study must be considered a clear antecedent and starting point for the present study, which intends to provide a new approach to determining the origin of As and its relationship with structural factors, thanks to a wider observation network.

In relation to the structural factors governing As distribution, it should be noted that the southern edge of the CDB is affected by very significant tectonic structures (e.g. the overthrust of SCS over the CDB, and the MPD). Recently, Rey-Moral et al. (2016) analyzed the regional gravimetry and magnetism in the area. The results corroborate the previous hypothesis, clearly identifying the prolongation of SCS fractures beyond the edge of the CBD (such as the Muñico Fault and MPD, aligned NE-SW (see Fig. 1b), as well as other NE-SW and NW-SW alignments. In that work, the distribution of As anomalies is clearly associated with the fracture landscape. Giménez-Forcada et al. (2016) established that high As and F concentrations in groundwater in the CDB could be explained by inflows of oxidizing alkaline groundwaters through major faults in the basement.

A similar context has been recognized in groundwater in other regions, for example in the geothermal area of the La Selva graben, NE Spain (Piqué et al., 2010; Folch, 2010), where CO_2-rich Na-HCO_3 hydrochemical facies enriched in As, Li, F, B and other dissolved species, such as silicic acid, are associated with an inflow of geothermal water through deep fractures. Forrest et al. (2013) recognized Na-Cl type waters with As, B, F and Li concentrations in excess of drinking-water standards in some wells in the Sonoma Valley (California) due to contamination by deep hydrothermal fluids.

Previous research in the study area and its surroundings found other trace elements associated with As in groundwaters, such as Cr, U and V (e.g. Sahún et al., 2003; Gómez et al., 2006; Vega et al., 2008; Giménez-Forcada and Smedley, 2014; Carretero, 2016). All of these elements may have their primary origin in the silicate minerals of the rocks of the SCS and the basement of the basin. Arsenic, Cr and V have a similar average crustal abundance and have an affinity to substitute Fe in minerals. Although the concentration of As in igneous rocks is usually low, maphic and ultramaphic rocks are enriched in V and Cr relative to most intermediate and silicic rocks. Conversely uranium is more abundant in silicic varieties of igneous rocks.

The majority of the silicate hydrolysis reactions produce silica, bicarbonate ions, clays and base cations. When As and associated trace elements substitute several cations in the primary silicate, they may end up in the final solution after hydrolysis or even be retained in the secondary mineral phases. Hot water has a high capacity to dissolve minerals in the host rock and, during mineral alteration, minor elements are released into the hot water leachate (Webster and Nordstrom, 2003). Therefore, in addition to the likely primary sources considered to explain high concentrations of As and other PTGTEs in groundwater, the existence of groundwater flows enriched in these trace elements must also be considered.

Arsenic is recognized as a carcinogen by the International Agency for Research on Cancer, IARC (WHO, 2009). The limit established by WHO for drinking water, and adopted by European legislation, is 10 μg/L (EC, 1998; WHO, 2011). Chromium (III) is an essential metal nutrient,