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ORIGINAL ARTICLE

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Naturally occurring arsenic in groundwater and identification of the geochemical sources in the Duero Cenozoic Basin, Spain

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Abstract Arsenic concentrations surpassing potability limit of 10 μg/L in the groundwater supplies of an extensive area in the Duero Cenozoic Basin (central Spain) have been detected and the main sources of arsenic identified. Arsenic in 514 samples of groundwater, having mean values of 40.8 μg/L, is natural in origin. Geochemical analysis of 553 rock samples, assaying arsenic mean values of 23 mg/kg, was performed. Spatial coincidence between the arsenic anomaly in groundwater and the arsenic lithogeochemical distribution recorded in the Middle Miocene clayey organic-rich Zaratan facies illustrates that the rocks of this unit are the main source of arsenic in groundwater. The ferricretes associated to the Late Cretaceous–Middle Miocene siliciclastics also constitute a potential arsenic source. Mineralogical study has identified the presence of arsenic in iron oxides, authigenic pyrite, manganese oxides, inherited titanium–iron oxides, phyllosilicates and organomineral compounds. Arsenic mobilization to groundwater corresponds to arsenic desorption from iron and manganese oxides and from organic matter.

Keywords Arsenic · Groundwater quality · Sedimentary rocks · Hydrochemistry · Cenozoic · Duero Basin · Spain

Introduction

The presence of arsenic in groundwater in pernicious concentrations for human health constitutes a worldwide high-priority groundwater quality problem (Duker et al. 2005). In many areas of the world, arsenic in the environment can be related to human activities such as base and precious metals mining and smelting, coal combustion, tanning waste, pigment production, pressure-treated wood, increased growth in feedlot-raised poultry and, in the past, to the use of pesticides (Nriagu 1994; Oremland and Stolz 2003). Arsenic pollution from these sources to groundwater tends to be mostly local. However, the main source for contaminating the drinking water aquifers all around the world is the naturally occurring arsenic. This arsenic can be sourced, among other causes, by geothermal and volcanic activities, aquitards mainly composed of clay-rich and/or organic-rich lithologies containing arsenic-rich minerals (e.g. arsenopyrite, pyrite, enargite) or aquifers containing iron and manganese oxides. These oxides show high affinity to arsenic and/or linked with sulphide minerals or organic carbon (Korte 1991; Nriagu 1994; Schreiber et al. 2000; Smedley and Kinninburgh 2002; Stollenwerk 2003).

In Spain, the presence of naturally occurring arsenic in groundwater has been reported in the sedimentary Duero and Tajo Cenozoic basins, located in central