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Investigation of the nature and origin of the geological matrices rich in selenium within the Hydrogeological Experimental Site of Poitiers, France

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ABSTRACT

The selenium (Se) content and the associated release mechanisms in both surface and groundwater have become a major concern worldwide over the past 30 years. Within the Hydrogeological Experimental Site of Poitiers (HESP), a large range of aqueous Se concentrations (from non-detectable to more than 30 ppb) is observed in a limited area (about 10 ha), where water flows are highly characterized. This site thus consists of an interesting spot to better understand the release mechanisms of selenium into groundwater. The present study consists of an identification and a characterization of the lithological sources of Se within the HESP. Total rock analyses applied to core samples from different depths and wells demonstrated that selenium is concentrated in argillaceous sediments enriched with organic matter, pyrite and uranium that fulfill a part of the karst cavities developed within the Bajocian host rocks. Mineralogical and petrographic investigations highlighted the heterogeneity of these filling materials and showed the presence of successive deposits under different climatic conditions. Extensive characterizations dated the selected Se-rich samples from the Upper Cretaceous and converged to demonstrate the external and continental origin of the studied filling materials and their transformation after deposition under reduced conditions. Only indirect correlations allow considering an agreement between the Se history and the very mature organic matter identified in the argillaceous samples. This association will be further favored to determine the mechanisms releasing selenium into groundwater.

1. Introduction

Although average selenium concentrations in the continental crust are relatively low (0.05 ppm), diffuse geogenic pollutions are widely observed (Coleman and Delevaux, 1957; Yang et al., 1989; Presser et al., 1994; Seby

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et al., 1998). Selenium is in fact an important micronutrient with a narrow range between its toxic and deficiency concentration (Barron et al., 2009; Levander and Burk, 2006). Se intake for animals and humans is mainly provided by meats, cereals and, to a lesser extent, by drinking water (Appleton et al., 2006). Human intake is indirectly related to the selenium content in natural waters and to the bioavailable fraction of selenium in soils and geological materials that can be easily transferred to water and biota.

The geographical distribution and availability of Se in soils and natural waters is largely uneven and linked to the variable concentrations in rocks, as already recently emphasized by Schmitt et al. (2012) for other elements such as Mg, Ca, Li, and B, and for their isotopic signature. Limestone, sandstone, mafic and ultramafic rocks, intrusive and extrusive acid rocks often contain low Se concentrations (Coleman and Delevaux, 1957). In contrast, coals, shales, argillaceous sediments and phosphate rocks could be enriched with selenium (Coleman and Delevaux, 1957; Fernández-Martínez and Charlet, 2009; Vesper et al., 2008).

Selenium can thus be highly concentrated in black organic-rich shales and seleniferous black shales that are the geological parent material of the widespread seleniferous soils in the United States and in Europe (De Temmerman et al., 2014).

In natural waters, selenium concentrations are generally lower than 1 ppb (Ralston et al., 2008), but may significantly increase, influenced by anthropic or geogenic sources to reach toxic levels (Charlet et al., 2007; Fernández-Martínez and Charlet, 2009). The main aqueous selenium chemical speciation corresponds to the most labile and bioavailable forms: the oxyanions selenites (Se^{IV}) and selenates (Se^{VI}) (Ralston et al., 2008). Selenium speciation strongly depends on pH and Eh (Masscheleyn et al., 1990). Hence, selenium has a complex behavior and a large variety of selenium compounds may be found in the environment (Fernández-Martínez and Charlet, 2009; Masscheleyn et al., 1990; Ralston et al., 2008; Seby et al., 1998).

In France, the selenium concentration limit for safe drinking water has been set at 10 ppb, but in several areas this limit is exceeded (Chabart et al., 2006; Gourcy and Winckel, 2010; Karnay, 1999; Vernous et al., 1998). In the East and the West of the Paris Basin, geogenic sources of Se were identified and the enrichment of water by Se is considered as a result of oxidation processes after the drilling of wells (Gourcy and Winckel, 2010; Gourcy et al., 2011). In the French Department of Vienne, selenium anomalies (up to 40 ppb) were observed in different water distribution units and were attributed to the presence of continental selenium-rich facies formed by gravels and silty clay (Barron et al., 2009; Karnay, 1999).

This work presents a study that aims to identify and characterize the potential lithological source of selenium in the well-characterized limestone aquifer of the Hydrogeological Experimental Site of Poitiers (HESP), France.

2. Settings

The Hydrogeological Experimental Site of Poitiers (HESP) is a field research facility whose primary objective is to support the development of characterization methods and modelling approaches for groundwater flow and solute transport in heterogeneous carbonate aquifers, as a basis for the protection and management of groundwater resources. Hydrogeological and hydrogeochemical investigations focus on a confined limestone aquifer, which has been extensively characterized over an area of approximately 10 ha.

The HESP is located in a geological area called "Poitou Threshold" (Gabilly and Cariou, 2007), which makes the transition between two large Mesozoic–Cenozoic sedimentary basins, i.e. the Paris Basin to the northeast and the Aquitaine Basin to the southwest (Fig. 1). The Poitou Threshold consists of Jurassic carbonate rocks lying on a Hercynian crystalline basement. On the HESP area, the sedimentary cover begins with around 20-m-thick Aalenian dolomitic limestone and dolomite. These facies are overcome by the Bajocian limestone formations (50–60 m). Bathonian and Callovian rocks were completely eroded southward Poitiers, and the Cretaceous sedimentary formations are completely eroded in the region.

Karst cavities partially filled with dark deposits are also present, and evidences based on the directional analysis of cave maps (Bodin and Razack, 1997) support the occurrence of karstification after the Cenozoic Pyrenean and Alpine tectonic phases.

Two limestone aquifers of regional extent occur in the Jurassic carbonate series:

- the Lower- and Middle-Lias aquifer;
- the Dogger aquifer.

These two aquifers are separated by the Toarcian aquitard consisting of low-permeability marls. The thickness of the Lower- and Middle-Lias aquifer is about 25 m, whereas the Toarcian aquitard and the Dogger aquifer are around 10 and 100 m thick, respectively. Previous works have demonstrated that these two aquifers are well isolated from each other by the Toarcian marls (Bodin et al., 2012; Chatelier et al., 2011). Furthermore, the coupling between flowmeter logs, borehole imaging logs

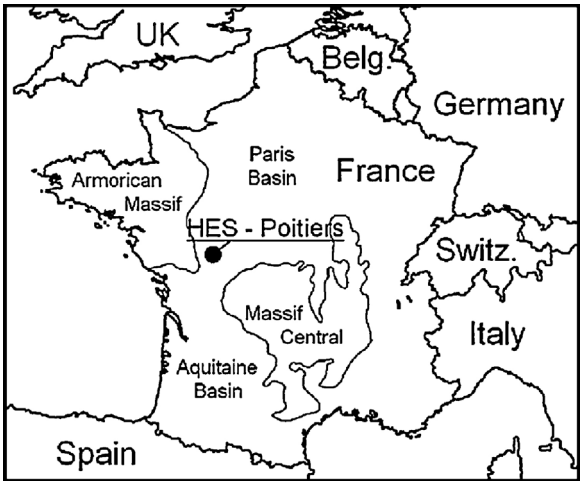

Fig. 1. Location of the HESP in France.