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The nature of Selenium species in the Hydrogeological Experimental Site of Poitiers

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Abstract

High concentrations in selenium - above the quality limit of 10 ppb - were detected in some wells of the Hydrogeological Experimental Site (HES) of Poitiers. Speciation measurements show that Se migrates mainly as selenate in the Dogger's aquifer water. The characterizations of drill core samples tend to attribute a geogenic origin to the selenium species observed in the Dogger's aquifer and to identify specific argillaceous levels fulfilling some karst cavities as selenium host matrix. Chemical extractions applied to these argillaceous samples show that most of Se is mobilized in parallel with the base-soluble organic matter part as Se(IV) species and other reduced forms.

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Keywords: Selenium, limestone aquifer, chemical extractions, speciation, argillaceous sediments.

1. Introduction

Selenium (Se) is a trace element essential for a healthy human body. The range between toxicity and deficiency concentrations in selenium is however very narrow. The Recommended Dietary Allowance (RDA) and the tolerable Upper intake Level (UL) for humans are so equal to 55 µg per kg and 350 µg per kg, respectively¹.

The chemical properties of Se are relatively similar to those of sulfur. Its speciation is highly dependent on the pH and Eh^{2,3} inducing a complex behavior and a large variety of selenium compounds in the environment. Se has four stable redox states: selenide (Se (-II)), elemental selenium (Se (0)), selenite (Se (IV)) and selenate (Se (VI))⁴⁻⁶. Selenate is predominant at circumneutral pH and high redox conditions as the oxyanion SeO_4^{2-} . It is the most soluble

specie of selenium with low capacities of adsorption and precipitation^{6, 7}. In the moderate potential range, selenites as H_2SeO_3 , HSeO_3^- or SeO_3^{2-} are the dominant species and their mobility is mainly governed by sorption/desorption processes^{4, 5}. Elemental Selenium is sparingly soluble and can exist as many allotropes or amorphous phases^{3, 4}. Selenides are thermodynamically stable under strong redox conditions and form a large variety of insoluble metals selenides compounds. Reduced selenium could have other forms such as H_2Se produced by a microbial process or non-volatile organic selenides such as seleno amino-acids^{4, 6}. The Se environmental cycle is moreover mainly controlled by slow redox reactions mediated mostly by microorganisms that allow many Se compounds to be found simultaneously in rocks and sediments⁶.

In natural waters, selenium concentrations are generally less than $1 \mu\text{g}$ per L^5 but may increase significantly in presence of natural and anthropic source of $\text{Se}^{4, 8}$. The issue of toxicity of selenium in drinking water has been debated since the 1970s. Different guidelines have been adopted by different institutions and countries. The upper limit of Se in drinking water is therefore currently set to $10 \mu\text{g.l}^{-1}$ by the European Union and most of the countries, $1 \mu\text{g.l}^{-1}$ as selenium trioxide by the Russian Federation, $50 \mu\text{g.l}^{-1}$ by the U.S. Environmental Protection Agency and $40 \mu\text{g.l}^{-1}$ by the World Health Organization (WHO) guidelines for drinking water⁹.

Se concentrations above the French upper quality limit (10 ppb) were detected in many wells used for drinking water production in several French Regions¹⁰⁻¹³. In the Department of Vienne, Se anomalies (up to 40 ppb) were observed in some water distribution points, inducing to close many wells and to proceed to expensive dilutions between wells¹⁴. The present study is focused on the dynamics of selenium at the scale of the Hydrogeological Experimental Site (HES) of Poitiers (Vienne). This paper especially consists of the identification of the source(s) of selenium in the HES.

2. Geological setting

The Hydrogeological Experimental Site (HES) of Poitiers is one of the five HES in France and is part of the H+ network - implied in a French Critical Zone network called CRITEX program. It is implanted in the Vienne department, 2 Km southeast of Poitiers in a geological area called Poitou Threshold. The primary purpose of the HES 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 groundwater resources. Investigations performed in the HES focus on a confined limestone aquifer which has been extensively characterized over an area of approximately 10 ha. The characterization included hydrogeophysical-well logging, hydraulic tests, core logging, and hydrogeochemistry.

The Poitou threshold is a middle altitude plateau (100-130 m) located between the Central Massif at the southeast and the Armorican Massif at the northwest and where the Mesozoic-Cenozoic sedimentary basins of Paris (Northeast) and Aquitaine (Southwest) met. The sedimentary succession in the Poitou Threshold can be summarized by a Hercynian crystalline basement covered by Jurassic carbonates rocks. Two limestone aquifers are formed in the Jurassic series: the lower and middle-Lias aquifer (5-200 m thick) and the Dogger aquifer (50-200 m thick). Low-permeability marls of the Toarcian provide the separation of the two aquifers. The experiments in the HES focus on the Dogger aquifer.

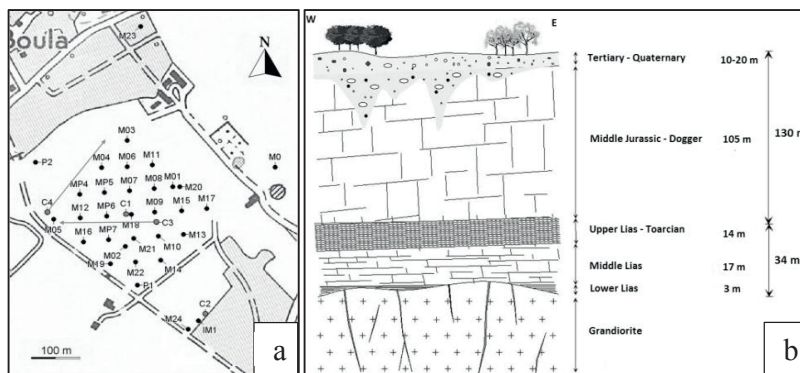


Fig. 1. (a) The locations of the wells in the HES; (b) Brief geological section at the HES.

Drilling campaigns were extended from 2002 to 2005 in the HES in a square area of 210 m x 210 m. Two types of drilling methods were used to install the wells: most of them (32 wells) were drilled in destructive mode and five other wells were cored to a diameter of 120 mm in 2003 (wells C1 and C2), 2006 (wells C3 and C4) and 2012 (well C5).

3. Results

3.1. The Se in the HES water

HES water sampling campaigns (April 2007, June 2007, March 2009 and June 2012) have partially investigated the chemical composition of the HES groundwater. The water of the supra-toarcian aquifer (Dogger) is typically calcium-bicarbonated. The total Se concentrations exceed the upper quality limit adopted in France (10 ppb) in 5 wells and vary from a well to another from few ppb to 25 ppb. This variation in such a small scale may be interpreted as the result of differences between the geological nature of the boreholes walls and the hydraulic connexions between the HES wells.

The speciation of Se in water samples from different depths of different wells - collected during June 2012 - was measured using HPLC-ICP-MS. Approximately 90% of the total Se revealed to be selenate species (SeO_4^{2-}), independently of the depth and of the well.

3.2. The origin of Se in the HES

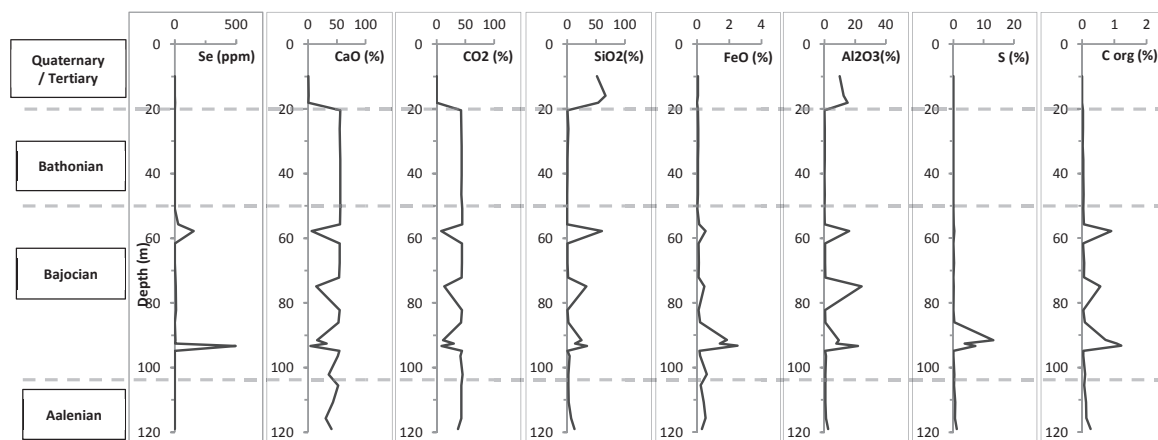


Fig. 2. Whole rock analysis results

Whole rock analyses were performed on thirty samples representing all the geological facies from the cored well C4. Partial data are graphically presented in Fig. 2. Positive anomalies in selenium can be observed in some levels that present both depletion of CaO and CO_2 and enrichment in SiO_2 and Al_2O_3 . These levels are thus attributed to argillaceous sediments in which aluminosilicates consist the most abundant phase. The depth of these levels also correspond to the three main karst cavities (50 m, 80 m and 110 m) identified by Audouin et al.¹⁵ and are defined as the most probable carrier matrix of selenium in the Dogger's aquifer.

The argillaceous levels rich in Se are also enriched with many elements including Fe(II), total sulfur and organic carbon. The association of selenium with organic matter and/or pyrite was described by many authors¹⁶⁻¹⁸, and such associations can be envisaged in the studied samples. Nevertheless, the correlations between selenium and Fe(II), S and organic C are moderately strong, suggesting more complex associations.

A Comparison between the diffractograms of the argillaceous samples and the detritic phases present in the limestone showed important mineralogical differences probably inducing an external origin of the clayey samples and not a simple dissolution of limestone in karst cavities. Petrographic and palynological investigations combined

with a molecular characterization of the organic matter present in the samples tend to confirm an external filling of the karst cavities.

3.3. The speciation of Se in the black shale

A six steps sequential extractions scheme developed by Martenz and Suarez¹⁹ and modified by Wright et al.²⁰ was applied to fresh black argillaceous samples from the C5 well of the HES. After each extraction, the total extracted Se was measured by ICP-MS, the Se speciation by HPLC-ICP-MS, the Total Organic Carbon (TOC) by a TOC analyzer and the extracted Al, Si, Ca and Fe by Atomic Absorption Spectroscopy.

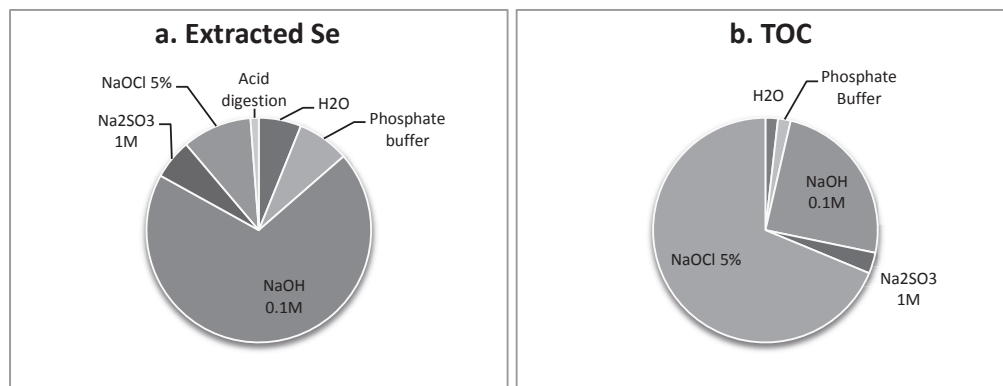


Fig. 3. Extracted (a) Se and (b) TOC by the steps of the Sequential Extractions Scheme

The dissolution of the mineral fraction of the samples was negligible during the extraction processes except for acid digestion.

The extractions with osmotic water (H₂O, used to extract the soluble fraction of Se) and the phosphate buffer (K₂HPO₄/KH₂PO₄, pH=7, used to extract the exchangeable fraction of Se) showed that the most soluble and bioavailable fraction of Se consist around 10% of the initial total Se. No significant amounts of organic carbon were dissolved in parallel.

Most of the total Se (around 70%) was extracted in very basic conditions, also inducing the extraction of around 25% of the initial organic carbon. An association between selenium and base-soluble organic matter is thus probable.

This assumption was confirmed by the extraction with the oxidative agent NaOCl. Only 10% of the total Se and more than 70% of TOC were dissolved in parallel, showing that a specific part -base soluble- of the organic matter carries selenium species.

Speciation measurements showed that an important part of the dissolved selenium is composed of Se(IV) species. An important part of the base-soluble selenium species as also not identified by HPLC-ICP-MS and are attributed to organic or reduced forms of selenium.

4. Conclusion

Whole rock analyses combined to mineralogical, petrographic and palynological studies were performed on different geological facies of the C4 well from the HES of Poitiers to tend to determine the origin of selenium in the Dogger's aquifer. Specific argillaceous levels fulfilling karst cavities revealed probable main selenium host matrix. Sequential chemical extractions performed on samples from this matrix showed that the base-soluble part of the organic matter contained in the samples is the main host of selenium. Mobilized selenium species via the experimental extractions are mostly selenites (HSeO₃⁻) and more reduced forms while selenium is mainly present as selenates in the groundwater of the HES. Additional studies will be performed to elucidate the mechanisms of liberation of selenium from its host geological matrix to the aquifer water and then better understand the behavior of selenium at the scale of the HES of Poitiers.

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