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Distribution and speciation of selenium in the black shale of the Dogger aquifer in the Poitiers Experimental Hydrogeological Site

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Selenium (Se) is an element having the narrowest range between dietary deficiency and toxic concentrations. In the environment, selenium has four oxidation states (-II, 0, IV and VI) and has a complex biogeochemical cycle. The European and French legislations fixed 10 μg/L as safe upper limit in drinking water. In several French regions2, selenium concentrations above the limit were detected in groundwater. This poses a problem for local authorities which are obliged to stop the exploitation of many wells.
In the north flank of the "Seuil du Poitou", Selenium concentrations above 10 ppb were measured in groundwater samples collected from five wells of the Poitiers Experimental Hydrogeological Site (SEH), which investigates a 100 m carbonate aquifer (Dogger). Total rock analysis applied on samples representing all the geological facies observed in the SEH show that selenium is concentrated in the black clays that fulfill some karst cavities; these clays are thought considered as the main selenium source in the Dogger Aquifer.
The main objective of this work is to study the distribution and the speciation of selenium in the geological matrix and the release mechanisms of Se in order to provide quantifiable data to numerical modeling of selenium's reactive flows across the aquifer. The distribution and the speciation of selenium in these black clays were studied by applying parallel and sequential chemical extractions and by verifying the impact of these extractions on the solid dissolution and organic matter mobilization. In all the extractions, the total dissolved selenium was quantified using ICP-MS and the selenium speciation in the aqueous phase by HPLC-ICP-MS. Verifying the impact of the extractions on the solid dissolution and on the organic matter mobilization was performed by measuring Al, Si, Fe and Ca by AAS and the Total Organic Carbon TOC and by acquisition of XRD diffractograms of the solid residues. Our results showed that most of the selenium is majorly associated with the soluble humic-like organic matter. 40% of extracted selenium identified as Se (IV), which was rarely observed in the literature and suggests that the Se in the black clays may be easily solubilized.
Keywords: selenium, speciation, distribution, black shale, chemical extractions, groundwater.