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## Lead isotope systematics in groundwater: implications for source tracing in different aquifer types

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### Abstract

We report Pb isotope measurements for 23 groundwater samples collected at different sites in France located from various types of aquifers (alluvial, sedimentary, karst, sand, volcanic and crystalline lithologies). We have measured the range of Pb isotopic variations in these groundwater samples in order to test the usefulness of Pb isotopes as a tool for tracing Pb sources in aquifer systems. In these groundwater samples, Pb isotopic ratios ranged from 17.33 to 18.56, from 15.45 to 16.11 and from 37.06 to 40.35, respectively for  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ ,  $^{208}\text{Pb}/^{204}\text{Pb}$ , whereas the Pb concentrations were between 0.023 and 0.160  $\mu\text{g/L}$ , and below the 10  $\mu\text{g/L}$  maximum allowable concentration of Pb in drinking water. Lead isotope ratios of the study groundwater display very large variations, in particular for the sedimentary aquifers. The Pb isotopic variations were not related to lead concentrations nor to the type of aquifers. The data indicate that Pb in groundwater is typically originated from the mixing of natural and anthropogenic sources.

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### 1. Introduction and objective of this study

Assessing the occurrence of lead and its isotopic variations in groundwater is important for identification and regulation of trace elements in aquifer systems. Lead could occur both naturally and/or as a result of human activities, and has important health implications upon exposure to levels above threshold values in drinking water. This was part of the Water Framework Directive<sup>1</sup> of the European Union that sets objectives for groundwater quality, and a list of 33 priority substances was adopted in 2001, in which Pb and its compounds were included. Therefore, it is essential to establish innovative tools such as isotope tracers for studying groundwater contamination and informing policy makers in the scope of water resources management.

Lead isotope data have been widely used to constrain the sources of Pb in the environment and particularly to identify the anthropogenic input from leaded gasoline and Pb mining activity. Since many years, it has been also shown in a number of studies, that Pb isotope compositions can provide an ideal tracer for applying in water quality

management. This is because Pb can be derived from both geogenic and anthropogenic sources, which may have very different Pb isotopic signatures. Pb isotopes have also proven to be an important and powerful tool in investigations of many aspects of hydro-geology.

In the present work, following a method developed by BRGM group for the direct measurement of low Pb level samples<sup>2</sup> and after a study of small monolithological aquifers in India<sup>3</sup>, we investigated the origin of Pb in French groundwater by using the Pb isotopic variations. Because of the large variability in hydrogeological settings of aquifers that could affect the occurrence and distribution of Pb isotopes in groundwater, the ability to use Pb isotopes as an efficient tool for groundwater characterization is limited. Therefore, the main objective of the present study is to characterize the Pb and its isotopes distribution in groundwater sampled from different aquifer types in France.

## 2. Samples and analytical methods

Twenty three groundwater samples representing six main aquifer lithologies were collected throughout France. The primary objective of the sampling strategy was to represent the larger spectrum of geological bedrock types and thus to investigate the diverse range of aquifer types.

In accordance with the aquifer types established in the guidance on groundwater monitoring for the Common Implementation Strategy of the Water Framework Directive, we sampled the following types of aquifers (Fig. 1): (1) an alluvial plain sediment aquifer, (2) consolidated sedimentary aquifers (in limestone and chalk rocks), (3) karstic aquifers, (4) sandy aquifers, (5) volcanic rock aquifers, and (6) weathered and fresh crystalline bedrock aquifers (including metamorphic rocks).

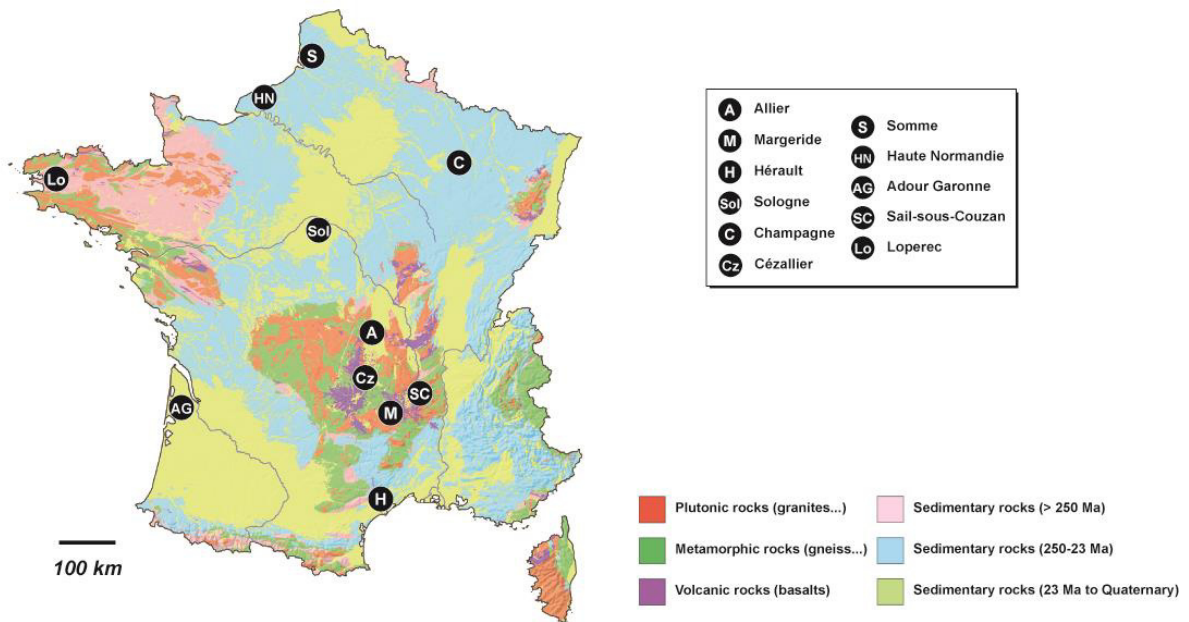


Fig. 1. Geological map of France and location of the groundwaters collection sites from this study.

A primary necessity in attempting to understand the distribution of Pb in groundwater is the accurate measurement of Pb isotope composition. However, the very low levels of Pb in groundwater present a considerable analytical challenge. For this study, measurement of lead isotopes was performed using a Neptune MC-ICP-MS which allows the simultaneous measurement of  $^{202}\text{Hg}$ ,  $^{204}\text{Pb}$ ,  $^{207}\text{Pb}$ ,  $^{206}\text{Pb}$  and  $^{208}\text{Pb}$  by using the fixed array, multi-ion counter system (MIC) installed in this instrument.

We performed the direct measurement of a solution containing 0.1  $\mu\text{g/L}$  of lead without any sample preparation beforehand (i.e., without chemical separation of the matrix). Only dilution or pre-concentration by evaporation (on an hot plate) of the sample were used to adjust the concentration of the solution to 0.1  $\mu\text{g/L}$  of lead in 3% v/v sub-boiling  $\text{HNO}_3$ . The method of direct measurement was initially developed in BRGM laboratory<sup>2,3</sup> and we have clearly evidenced that sample matrix does not have a significant effect on the analysis if the total cationic charge is less than 400 mg/L (Na + Mg + Ca + K).

### 3. Lead isotopes in groundwater

Dissolved lead in groundwater can have different origins: Pb can either be derived from the water/rock interactions within the aquifer rocks, or from an anthropogenic source (e.g., surface industrial or agricultural activities). Since many years, it has been well established that Pb isotopes can be successfully used as tracers of hydro-geologic processes, particularly in environments where contamination from anthropogenic Pb sources has been evidenced<sup>3-8</sup>.

In Fig. 2, Pb isotopic compositions for the groundwater samples are presented in conventional Pb-Pb diagrams ( $^{207}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$ ). In these figures, we also illustrate the fields that represent different Pb source 1) natural Pb in the aquifers (i.e., pre-industrial sediments of French rivers<sup>4</sup>); 2) the mean Upper Continental Crust (UCC)<sup>9</sup>; 3) industrial Pb in France<sup>4</sup>; and 4) Pb from gasoline (derived from alkyl Pb compounds added to petrol as antiknock agent<sup>10</sup>).

The Pb-Pb diagrams (Figures 2a and 2b) clearly show that Pb in the study groundwater originated from the mixing of natural and anthropogenic sources, and more than two sources are needed to explain the whole range of the isotopic variations. Moreover, for higher values of  $^{208}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$  ratios, we should also consider the dissolution of U-rich and/or Th-rich minerals present in the aquifer for naturally occurring source of Pb.

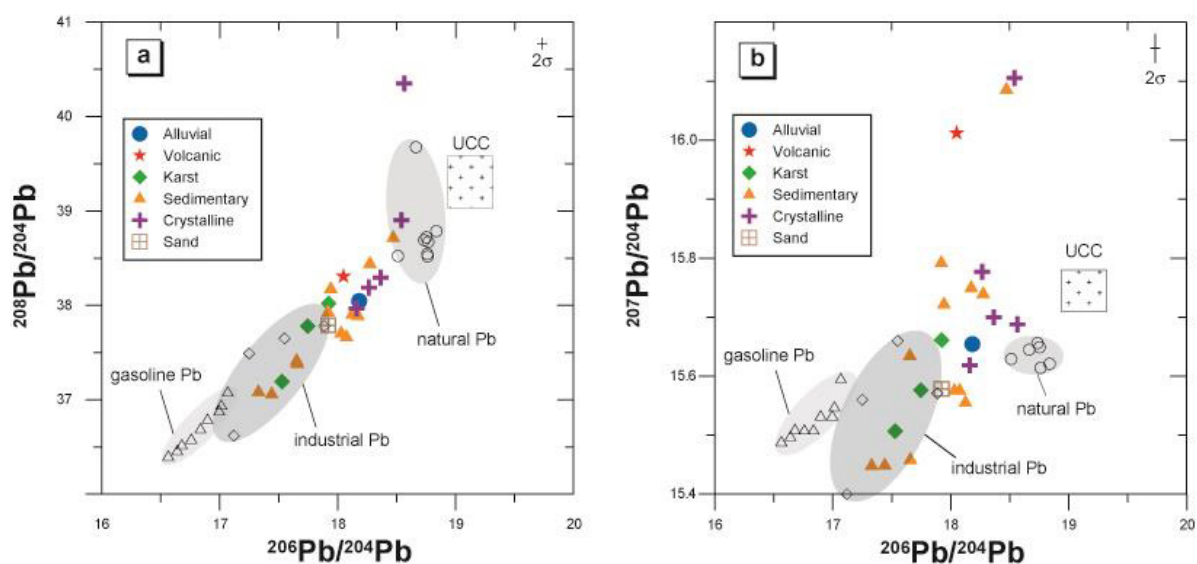


Fig. 2. Pb-Pb diagrams ( $^{208}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$ ). Mean uncertainties for isotopic ratios are reported for comparison in the upper right part of each diagram.

Indeed, radiogenic values for  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios were measured in some samples reflecting the relative contribution of U-rich and/or Th-rich minerals during water/rock interactions that occur within the aquifer. This latter feature could be explained by the fact that during water/rock interaction, accessory minerals are able to release Pb in the groundwater more easily than dissolution of Pb from the whole host rock. In addition, these minor

mineral phases may contain considerable concentrations of incompatible elements (including U and Th), and therefore high concentrations of radiogenic Pb<sup>3</sup>. Hence, the range of Pb isotopes in groundwater reflects not only the bulk signature of the host rocks but also the contribution of the secondary minerals with different U/Pb and Th/Pb ratios relative to the host rocks.

In addition, the isotopic differences between minerals increases with time due to the radiogenic decay through time of <sup>238</sup>U to <sup>206</sup>Pb, <sup>235</sup>U to <sup>207</sup>Pb and <sup>232</sup>Th to <sup>208</sup>Pb. While Pb isotope ratios are not fractionated during water/rock interactions, radiogenic isotopic signatures in groundwater may differ from whole rock Pb isotope signature because different secondary minerals could undergo congruent or incongruent dissolution at different rates<sup>3,11</sup>. Thus, the isotopic composition of groundwater will differ from the host rock, reflecting the timing and intensity of water-rock reaction and differential mineral solubility. This is the reason why the combination of thorogenic (<sup>208</sup>Pb) and uranogenic Pb (<sup>206</sup>Pb, <sup>207</sup>Pb) is especially useful for discriminating Pb isotope sources. Therefore, it is recommended that all four Pb isotopes, normalized to <sup>204</sup>Pb, should be used to delineate groundwater Pb contamination.

#### 4. Conclusions

In this study, we have measured the range of Pb isotopic variations for 23 groundwater samples collected at different sites in France located from various types of aquifers. Pb isotopic ratios ranged from 17.33 to 18.56, from 15.45 to 16.11 and from 37.06 to 40.35, for <sup>206</sup>Pb/<sup>204</sup>Pb, <sup>207</sup>Pb/<sup>204</sup>Pb, and <sup>208</sup>Pb/<sup>204</sup>Pb, respectively, whereas the Pb concentrations were between 0.023 and 0.160 µg/L, below the 10 µg/L maximum allowable concentration of Pb in drinking water.

Lead isotope ratios of the groundwater of the present study display very large variations, in particular for the sedimentary aquifers. The Pb isotopic variations were not related to lead concentrations, nor to the type of the aquifers. Groundwater samples from granitic aquifers had generally the highest radiogenic values, which may be due to differential weathering of U- and Th- bearing minerals. Pb isotope tracing clearly shows that Pb in groundwater results from the mixing of natural and anthropogenic Pb sources, and more than two sources are needed to explain the whole range of the data. For detecting the natural source of Pb in groundwater this study shows that the dissolution of U- and Th-rich secondary minerals can contribute Pb to groundwater with different isotopic ratios of the whole rocks from the aquifers. Consequently, it is strongly recommended that all four Pb isotopes will be investigated in hydrologic and environmental studies.

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