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# Sediment dating and groundwater residence time in the lower basin of the Var river by radiochemistry and $\gamma$ -ray spectrometry methods

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Received 26 May 2008; accepted after revision 13 November 2008

Available online 4 January 2009

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## Abstract

A method for dating sediment core layers from the Var riverbed was developed. The signature of the Chernobyl event was detected in the layer sequence by  $\gamma$ -ray spectrometry of <sup>137</sup>Cs and correlated to the flow amplitude from the historical records.

The residence time of groundwater in the aquifer of the lower Var valley was determined by measuring activity ratios of radium isotopes in well water samples. **To cite this article:** V. Barci et al., *C. R. Chimie 12 (2009)*.

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## Résumé

Une méthode pour dater des carottes de sédiments collectées dans le lit du Var a été développée. L'évènement de l'accident de Tchernobyl a été détecté dans les échantillons par spectrométrie gamma du <sup>137</sup>Cs et corrélé avec les intensités des crues. Le temps de résidence de l'eau dans la nappe phréatique de la basse vallée du Var a été déduit des rapports d'activités des isotopes de radium dans l'eau de puits. **Pour citer cet article :** V. Barci et al., *C. R. Chimie 12 (2009)*.

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**Keywords:** Radiochemistry; Coprecipitation; Cesium; Radium; Gamma-ray spectrometry; Resource management

**Mots-clés :** Radiochimie ; Coprécipitation ; Césium ; Radium ; Spectrométrie gamma ; Exploitation des ressources

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## 1. Introduction

The knowledge of groundwater resources is becoming increasingly crucial owing to global warming, pollution risks and anthropogenic pressure. Large and reliable data banks of resource state and availability are needed by decision makers. We are carrying out a detailed study of the catchment basin of the Var river, which represents the main water supply of the Alpes-Maritimes department. In this paper we focus on the application of selected radiochemical and nuclear spectrometric methods to sediment dating and measurement of groundwater residence time. Sediments were collected in the riverbed and groundwaters were sampled in local wells. We report preliminary results of a first exploratory campaign.

## 2. Experimental methods

Radiochemical methods for radium isotope separation were applied. Radium, as an alkaline earth element, can exist only in the  $2^+$  oxidation state. Radium and barium are homologous elements in the alkaline earth group. Due to the similarity of their ionic radii, the chemical behavior of radium is very like that of barium. The  $(\text{Ba,Ra})\text{SO}_4$  coprecipitation has been shown to be an important process in controlling the solubility of radium in natural waters [1–7].

Water samples of about 200 L were collected, and acidified with 1%  $\text{HNO}_3$ . Radium was coprecipitated with 300 mL  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in aqueous solution (10 g/L). Common market reagent from Panreac was used in this test. The solution was stirred; the  $(\text{Ba,Ra})\text{SO}_4$  precipitate was dried and placed in a standard round box of  $9 \text{ cm}^3$  volume, sealed with adhesive tape.

Sediment samples were processed with no chemical preparation.

Gamma-ray measurements of the samples were carried out with two HPGe *p*-type detectors, 30% and 17% efficiency, manufactured by ORTEC, in a shielded environment with graded castle, 5 cm lead and 0.5 cm thick copper.

## 3. Sediment dating

The first application is sediment dating. Several dams were built across the banks in the lower course of the Var river in the 1970s; the rises and floods have filled the dams and offer a chronological record of past events. We devised to use the Chernobyl signature in 1986 to obtain a time mark in the

sediment sequence. The presence of  $^{137}\text{Cs}$  should be a clear footprint of the event. Cesium forms few stable complexes and is likely to exist in ground and surface waters as the uncomplexed  $\text{Cs}^+$  ion, which adsorbs rather strongly to most minerals, especially mica-like clays. The solubility of most cesium compounds in water is very high. In general, most soils absorb cesium rather strongly [8]. A core sample of about 9.5 m depth, 4 cm diameter, was collected at the dam number 4, at about 6 km upstream. The core was dried in air and cut by half lengthwise. Selected layers of 2–3 cm thickness were homogenized and counted by  $\gamma$ -ray spectrometry. Activity concentration versus depth is reported in Fig. 1. The activity maximum is present in a thin layer at about 4.20 m depth. It corresponds to a wide flood layer of about 40 cm thickness. Actually from April to June a strong flood event took place in 1986, just at the time of the Chernobyl accident (April 26), with flow rates well above  $100 \text{ m}^3/\text{s}$  (Fig. 2). Cesium is mostly present in clay sediments, and sand layers have very low cesium concentrations. This behavior agrees with the known properties of cesium as previously reported. The steep fall of cesium concentration at higher depth marks the transition to a sand layer. Each flood is characterized by a deposition pattern of coarse sand layers first followed by thinner particle clay layers, according to the decreasing strength of the flow current with time. At lower depth the concentration fall is slow and more regular and could indicate an effective decay pattern through the clay layers. Most of the Chernobyl fallout is concentrated in the first clay layer corresponding to the 1986 flood.

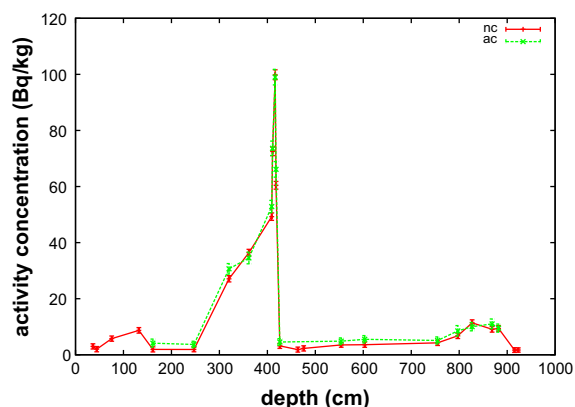


Fig. 1.  $^{137}\text{Cs}$  activity concentration at dam 4. The measurements were performed with two different detectors labeled *ac*, 17% efficiency, and *nc*, 30% efficiency.

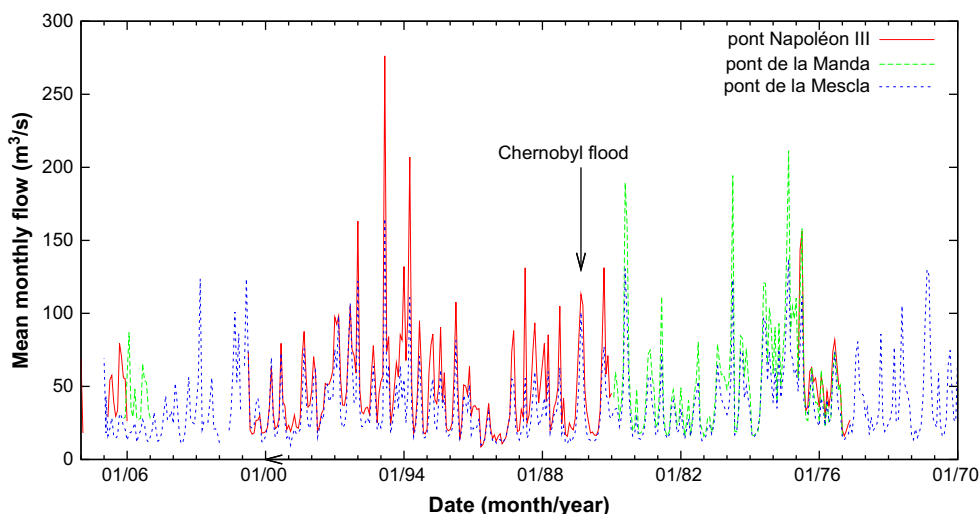


Fig. 2. Recorded monthly mean flow rates of the Var river<sup>1</sup>. The records of three measuring stations are reported: at the mouth of the Var (*pont Napoléon III*), halfway up the valley (*pont de la Manda*) and the upper Var valley (*pont de la Mescla*).

#### 4. Residence time of groundwater

The second application is the residence time of groundwater: the knowledge is of primary importance for resource renewal. The isotopic ratio of radium radionuclides could allow one to measure this parameter. Radium isotopes in nature are present as decay daughters from uranium and thorium families:  $^{224}\text{Ra}$  (half-life  $T_{1/2} = 3.66$  d) and  $^{228}\text{Ra}$  (5.75 y) from the  $^{232}\text{Th}$ ,  $^{226}\text{Ra}$  (1600 y) from the  $^{238}\text{U}$  and  $^{223}\text{Ra}$  (11.43 d) from the  $^{235}\text{U}$  family. The measurement of isotopic ratios at different locations of the underlying groundwaters should allow the measurement of the residence time if the following conditions are fulfilled: the activities are detectable; the value is in the range of one of the half-lives; and the process is reasonably close to external effects. Two wells, 10.8 km apart in the valley at Carros (site 1) and at Saint-Laurent-du-Var (site 2), were chosen for sampling, nearly at the top and bottom of the main aquifer.

The activity concentration of radium isotopes is related to the transport time  $t$  from site 1 to 2.

$$\text{Ra}_2 = \text{Ra}_1 \exp(-\lambda_{\text{Ra}} t) \quad (1)$$

Due to its long half-life the  $^{226}\text{Ra}$  activity may be supposed to be constant if the residence time is of the order of some years. Conversely  $^{223}\text{Ra}$  and  $^{224}\text{Ra}$  are short-lived and rapidly disappear. So the activity ratio between  $^{228}\text{Ra}$  and  $^{226}\text{Ra}$  should be:

$$\left( \frac{^{226}\text{Ra}}{^{228}\text{Ra}} \right)_2 \left( \frac{^{228}\text{Ra}}{^{226}\text{Ra}} \right)_1 \approx \exp(\lambda_{228\text{Ra}} t) \quad (2)$$

Using ratios instead of activity allows one to get rid of detector efficiencies, chemical yield, counting times, and correction factors and to take in account only bare count numbers. Actually, activity measurements are most effective with the decay daughters of radium isotopes, which possess the strongest lines, but decay equilibrium must be reached and intermediate gaseous radon isotopes need not escape from the sample. So one must wait for decay equilibrium and the sample must be sealed to prevent radon escape.

The box with the sample was sealed in a tight holder, the same inner dimensions as the box, and counted with  $\gamma$ -ray detector. Ten runs of 300,000 s each at 10-day intervals were carried out. No significant variation of the counting rate was observed with time delay. We may infer that the sealing of the plastic box with adhesive tape was probably enough to prevent radon escape, at least within experimental uncertainties. The gamma-rays from the daughter  $^{228}\text{Ac}$  at 910 and 970 keV energies were used for  $^{228}\text{Ra}$  activity determination, the gamma-rays from  $^{214}\text{Pb}$  at 295 and 352 keV for  $^{226}\text{Ra}$ . The background level of natural radioactivity was found relatively high, nevertheless, with a total counting time of about one month for each point, we calculated a ratio (Eq. (2)) of  $1.62 \pm 0.13$  for a transport time of

<sup>1</sup> Data obtained from [www.hydro.eaufrance.fr](http://www.hydro.eaufrance.fr).

$4.0 \pm 0.7$  y between the two sites. The residence time should be of the same order.

## 5. Conclusions

Some preliminary results of our investigation of the Var aquifer have been reported. The work is in progress to better characterize the time sequence of the sediment deposition; the flood thickness compared to the flow records should allow one to date the core layers. Further samplings are planned to obtain a closer description of the deposition history.

The background level of the detection device should be reduced: a better pure reagent,  $\text{Ba}(\text{NO}_3)_2$  99.999% purity from Aldrich has to be used in the next campaigns. The thickness of the lead castle will be increased to 10 cm.

The chemical procedure should be refined. A pre-concentration step has to be added to enhance chemical yield.

The model of groundwater transport should be improved. In particular, it should account for radium exchanges between water and solids in the aquifer

and for possible side contributions from secondary aquifers.

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