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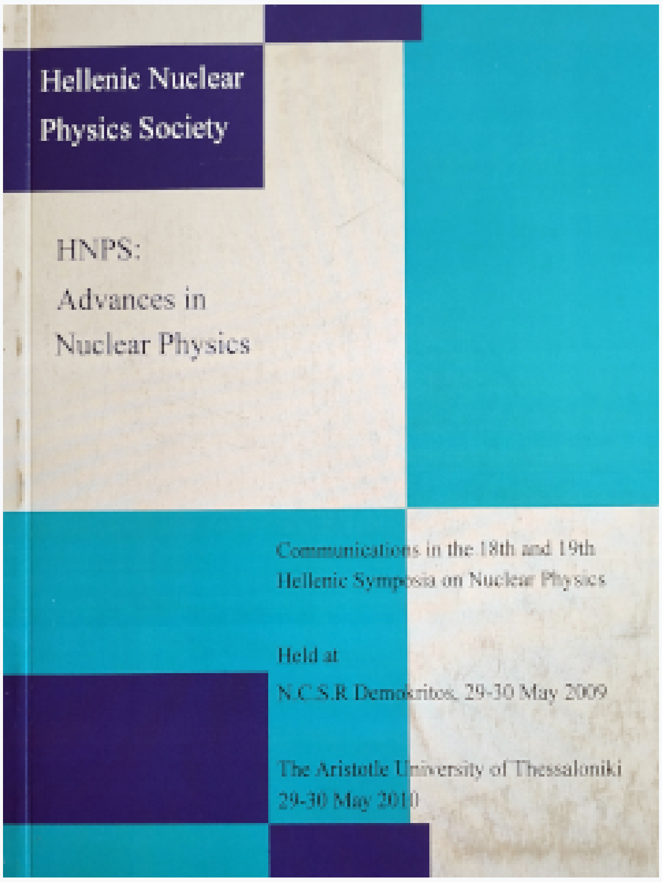

Gamma spectrometry technique for the determination of residence time in Submarine Groundwater Discharges

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Gamma spectrometry technique for the determination of residence time in Submarine Groundwater Discharges

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Abstract

The evaluation of time period that meteoric water remains in the ground (residence time) before exiting in the open sea can be a valuable information for the submarine groundwater discharges (SGD) in the costal zones. Coastal waters contain elevated dissolved activities of radium isotopes compared to the open ocean, where excess activities are zero. Lately it has been shown by Moore et al., that residence time can be estimated by a model based on radium radioisotopes ratio reduction throughout the coast. However the standard methods for the estimation of radium isotopes concentration in the water are sophisticated, time consuming or require big amount of sample. Hereby, a method based on the direct gamma ray spectrometry of untreated water samples from coastal areas is applied to determine the residence time of the SGD. Efficiency calibration of the spectrometry set up has been performed for two different volumetric sample geometries, using ^{152}Eu/^{154}Eu solution as reference source. In order to ensure the reliability of the method, the background courting rate magnitude and variance through time have been defined for the radioisotopes of interest. Additionally, the minimum detectible activity (MDA) of the measuring system was determined, in Becquerel per cubic meter, as a function of energy in water samples. The developed method was applied and validated for water samples from the submarine spring in Stoupa Bay, southwestern Peloponnesus. The defined residence time varies from 3 to 6 days, being in good agreement with the results of the standard geological pigment-tracer method.

Keywords: residence time; SGD; gamma ray spectrometry; HPGe; ^{224}Ra /^{228}Ra AR ; MDA; Stupa Bay

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1. Introduction

The last decades it has been clarified that Submarine Groundwater Discharges (SGD) are a phenomenon of crucial importance for coastal – inland hydrology and responsible for many oceanic and environmental processes. Only recently the use of radiotracers for the investigation of SGD has been established as a very effective scientific tool. Among the natural radiotracers, Radium isotopes can be considered as the most suitable, with various applications in oceanic, costal and estuary environmental studies [1, 2].

The time that groundwater remains underground before it exits at the costal seabed is a parameter of great interest, not only for understanding the local hydrology in regional scale, but the water cycle budget in wider scales. However, the quantitative approximation of this magnitude is rather complicated and not yet well established. Among many definitions, residence (or flushing) time of groundwater has been widely used in many field studies, where it can be derived through the ratio calculation of radium isotopes in water samples [3]. In specific, measurements of the radium radiotracers ^{224}Ra and ^{228}Ra with vast decay rate variance - 3.66 days and 5.7 years respectively - at the groundwater input coastal zone (Flux) and at the mixing/decay balance intermediate zone (Inventory) provide the ^{224}Ra /^{228}Ra activity ratio (AR) for samples isolated from fresh inputs of Ra. Residence time can then be calculated from the equation:

$$T_w = \frac{\left[F\left({}^{224}\mathrm{Ra}/{}^{228}\mathrm{Ra}\right) - I\left({}^{224}\mathrm{Ra}/{}^{228}\mathrm{Ra}\right)\right]}{I\left({}^{224}\mathrm{Ra}/{}^{228}\mathrm{Ra}\right)\lambda_{224}} \tag{1}$$

where λ_{224} is the is the decay constant of ^{224}Ra (0.19 d^{-1}). The model is based on the fact that both isotopes are lost from the system by mixing, but only ^{224}Ra is lost by radioactive decay, as well as the assumption that the system is in steady state so the mixing and decay terms along with fresh Ra inputs are incorporated into the residence time equation.

The standard techniques for the Ra isotopes concentration measurement are using water samples pre-concentration and/or infiltration in Ra-absorption filters, using α, β and, lately, γ spectrometry [4-6]. Although the above methods are steady and reliable, they are also time consuming, expensive and present sampling difficulties. In this work we investigate the possibility of indirect determination of the radium radioisotopes concentration in water, throw the direct measurement of natural water samples with high resolution HPGe detector. Assuming radioactive equilibrium, ^{224}Ra and ^{228}Ra ratio can be indirectly calculated by the gamma radioactive daughters ^{208}Tl and ^{228}Ac, respectively. Subsequently, residence time can be estimated from the equation (1), replacing the ^{224}Ra /^{228}Ra ratio by the ^{208}Tl/ ^{228}Ac ratio.

2. Materials and method

Two different volumetric containers of 0.615 L and 2.265 L, from high pressure toughness pyrex-glass, where used for the water samples collection. The samples where measured placed vertically on the window of a coaxial p-type high purity Ge detector (GEM-FX8530P4, Ortec®).

The detector was shielded surround by a lead layer with 23 mm height and 31 mm width. The energy and efficiency calibrations for the two geometries were performed using ^{152}Eu/^{154}Eu solution reference source [7]. Proportion of the source was dissolved in deionized water filling the two containers and the solutions were homogenized mechanically before they were measured for 1 h. The contribution of the ambient background radiation in the experimental spectrums was determined using phantom samples containing only deionized water, while measurements for various measuring times during 7 months period were analyzed (Fig. 2).

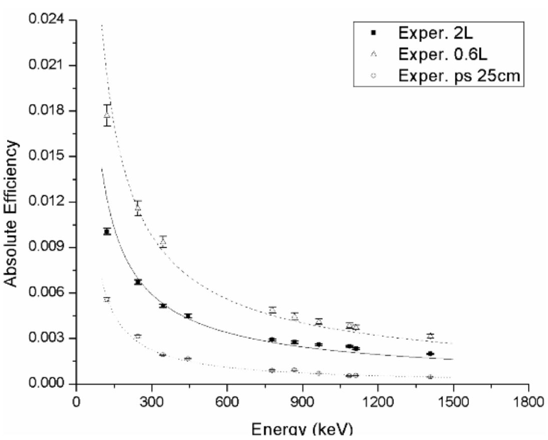

Fig. 1. Experimental efficiency curves of the detection system for point source in 25 cm distance from the detector and for extended volumetric sources (0.615 and 2.265 L) in contact with the detector's window.

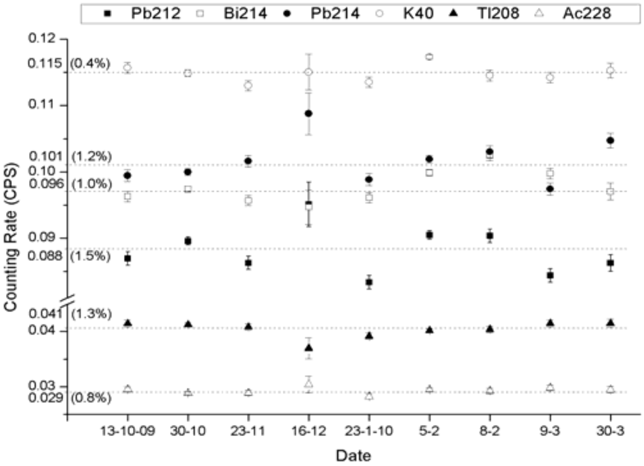

Fig. 2. Time variance estimation of the main background radioisotopes influence in the spectrum from their stronger photopeak.

The estimation of the residence time according the equation (1) demands the calculation of the ^{224}Ra /^{228}Ra ratio in one water sample from the SGD flux point and in another sample, from a typical inventory point. Taking into account that there is not any physical reason for selective enrichment of a particular isotope consequent ^{224}Ra and ^{228}Ra natural radioisotopes series it can be assumed radioactive equilibrium between the Ra isotopes and their progenies at the instant of the samples collection. The concentrations of ^{224}Ra and ^{228}Ra are then proportional to the concentrations of ^{208}Tl and ^{228}Ac, respectively, as well as and their ratios. ^{208}Tl and ^{228}Ac concentrations in the water samples can be derived from gamma ray spectrometry, namely from the counting rate of their more intense photopeaks – at 583.19 keV and 911.16 keV respectively – having subtracted the background spectral contribution in these energies. The ^{224}Ra /^{228}Ra ratio in each sample is then equal to the deviation of these two counting rates (e.g. $(^{208}\mathrm{Tl})_{\mathrm{cpd}}/(^{228}\mathrm{Ac})_{\mathrm{cpd}}$ for counts per day) multiplied with a constant that includes the photopeaks intensities and efficiencies. Finally, after of the deletion of this constant factor, the equation (1) becomes:

$$T_w = \frac{\left[F\left(\left({}^{208}Tl\right)_{cpd}\Big/\left({}^{228}Ac\right)_{cpd}\right) - I\left(\left({}^{208}Tl\right)_{cpd}\Big/\left({}^{228}Ac\right)_{cpd}\right)\right]}{I\left(\left({}^{208}Tl\right)_{cpd}\Big/\left({}^{228}Ac\right)_{cpd}\right)\lambda_{{}^{224}Ra}} \tag{2}$$

where λ_{224} is the is the decay constant of ^{224}Ra (0.19 d^{-1}).

For the residence time estimation two water samples from the flux and the inventory regions of the examined SGD were measured, along with background radiation correction. Because of the small Ra concentration in the environmental samples and in order to prevent the short lived ^{224}Ra loss, the measurements were performed in less than 5 days period from the samplings. Decay correction of the ^{208}Tl counting rate was also performed, taking into account the time between sampling and measurement, as long as the measuring time itself.

3. Study area

The aforementioned method was implied and tested at a submarine spring in the Bay of Stoupa, located in southwestern Peloponnese, in Messinia prefecture (Fig. 1). Many locations of submarine groundwater discharge are easily visible on the sea surface around the bay, while the largest groundwater source is located about 100 m offshore with a strong SGD emanating from fissures in the bedrock at roughly 25 m depth. The submarine spring was first reported in 1975, although local inhabitants claim that the spring have never stopped emanating water during, at least, the past 60 years. The study area is easily reached by a small boat and divers were recruited to grab water samples throughout one year period (2009 - 10). In each campaign, two water samples were collected directly from the spring exit (Flux) and from a random point of the water accumulation/mixing area (Inventory), at 25 and 10 m depth respectively.

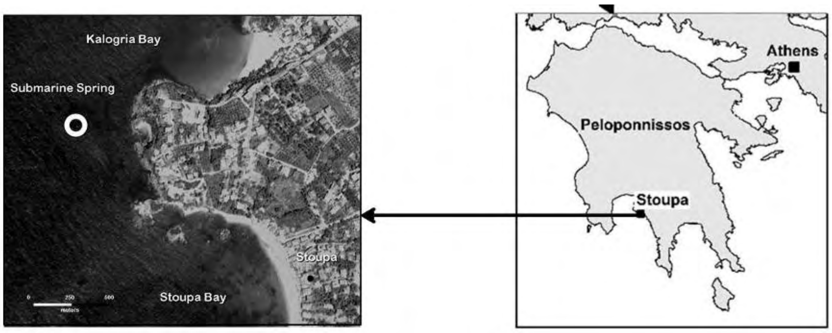

Fig. 3. The location of the studied costal submarine spring of Stupa Bay in southwestern Peloponnesus.

4. Results

The developed method was carried out in order to provide an alternative and effective way for the estimation of the residence time in costal SGD. The method's possibilities and limitations were examined by the determination of the minimum detectible activity (MDA) of the detection system. A comparison with a standard geological method was also performed for the estimation of the groundwater residence time of a submarine spring in Stoupa.

4.1. Minimum detectible activity

According to the analysis of the background radiation (Fig. 2), the variation of the counting rate for all important radioisotopes does not exhibit 1.5 %, for both extended geometries. However, the capability of the measuring system to detect additional radiation is also depend on the detector efficiency for the specific set up and the sample magnitude. Mathematically, based on the Currie formula [8], the minimum detectible activity (MDA) of volumetric water samples in Bq/m^3 is given by the equation [9]:

$$\mathrm{MDA} = \frac{L_D}{\varepsilon \cdot V \cdot I_\gamma \cdot T} \tag{3}$$

where L_D is the detection limit (in counts), T is the acquisition time (in sec), I_γ the emission probability of the detected γ-ray, V the volume of the sample (m^3) and ε is the absolute efficiency.

The mean MDAs have been calculated for the dominant ambient radioisotopes, by appling equation (3) to the data from the systematic analysis of the background spectrums for the two sample geometries, (Fig 4a). Additionally, the dependence of MDA from the time was also examined, by measuring deionized water samples for acquisition time varying from same hours to few days (Fig. 4b). From the results of the study it is shown that one day measurement of water samples placed in the big container are the more suitable set up form the needs of the developed method, achieving a ~2.5 Bq/L lower Ra concentration threshold.

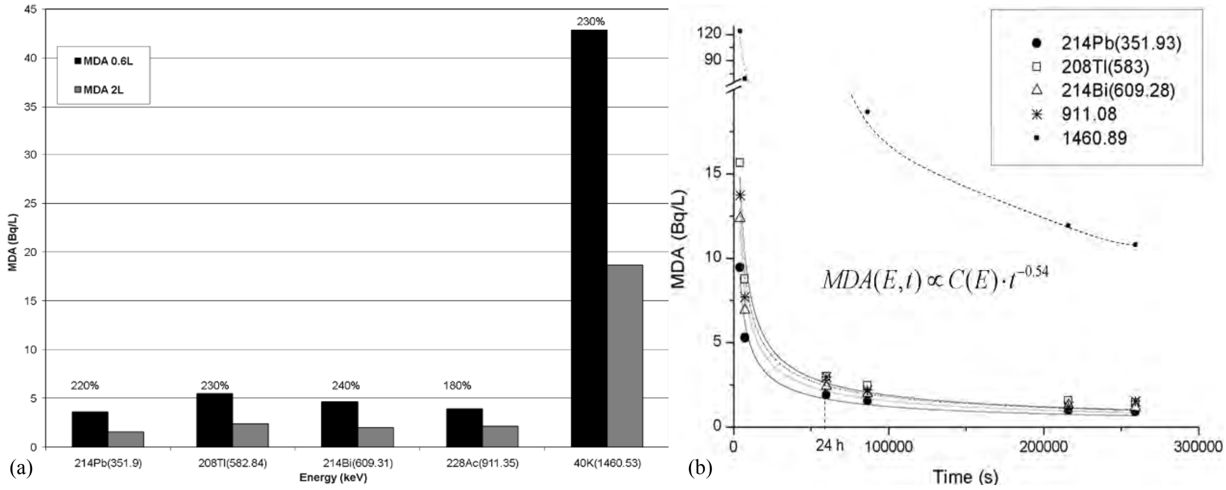

Fig. 4. MDA of some isotopes of interest calculated from their main photopeaks: a) comparison between measurement set up of the two water sample containers and b) dependence from the measuring time.

4.2. Models comparison

Samples from the submarine spring in Stoupa, from the flux and the inventory region were measured according the developed technique and the residence time was calculated (Table 1).

Table 1

Residence time estimation according the developed method (equation 2) of the submarine spring in Stoupa, for different sampling period.

Sampling date	8-Oct-2009	13-Nov-2009	18-Jan-2010	3-Mar-2010	23-Mar-2010	12-May-2010	12-May-2010
Residence time (d)	4.5 ± 2.4	5.7 ± 2.9	3.4 ± 2.0	4.8 ± 2.2	2.7 ± 1.8	3.8 ± 1.6	3.8 ± 1.6

The residence time varies from 3 to 6 days, while the mean value was found 4.6 ± 1.7 d for the period from Oct. 2009 to May 2010. The relative error of the estimation was approximately 50%, due to the low Ra activities in the water samples.

Experimental estimation of the residence time was also performed, using the standard geological pigment-tracer method. Namely, large quantity (~ 4 kg) of fluorescent substance (pigment) was shed at the nearest mountainous karst opening, where terrestrial flowing water sinks underground. Later on, samples from terrestrial costal springs were collected on regular base for several days, in which the concentration of the fluorescent substance was determined. The average residence time was calculated from the exponential decrease of the pigment concentration in the samples; and found to be approximately 5.5 d.

5. Conclusions and discussion

The developed method for the estimation of residence time in SGD described here is based on the direct gamma spectrometry of untreated water samples. The method is reliable for quantitative analysis of radium rich waters (> 2.5 Bq/L). For small concentrations the statistical errors rise up to 50%, though it can provide the upper threshold of the ^{224}Ra and ^{228}Ra activity. The comparison between the two different volumetric geometries shows that measurements of water samples with 2 L container are having reduced detection efficiency in all the gamma rays energy range than with the 0.6 L container, but they provide a MDA improvement by a factor of two for the radium isotopes. The application of the method in the Stoupa Bay submarine spring concluded with a annual mean residence time of 4.6 ± 1.7 d, being in very good agreement with the pigment-tracer method.

The main advantage of the described method is that it is straightforward, quick and economic, as requires a small amount of water samples and no chemical or physical samples treatment. From the other hand, it is strongly dependent from the sampling technique and point selection, as well as demands elevated radium concentration. Consequently, it can be said that the method is suitable and robust for point source SGD with nitense flux. The method is expected to be improved for further shielded detection system, while other geometries (e.g. Marinelli) can be tested in order to extend its applicability in more diffusive SGD cases.

Acknowledgments

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