

# RADIO ISOTOPES AS TRACERS FOR THE STUDY OF THE SUBMARINE GROUNDWATER DISCHARGE OF KALOGRIA BAY, SW PELOPONNISSOS, GREECE

C. Tsabaris<sup>1\*</sup>, D. Patiris<sup>1</sup>, K. Ioannides<sup>2</sup>, A. P. Karageorgis<sup>1</sup>, K. Stamoulis<sup>3</sup>, G. Eleftheriou<sup>4</sup>, D. Georgopoulos<sup>1</sup> and E. Papathanassiou<sup>1</sup>

<sup>1</sup> Hellenic Centre for Marine Research, Institute of Oceanography, 19013, Anavyssos, Greece - tsabaris@ath.hcmr.gr

<sup>2</sup> University of Ioannina, Nuclear Physics Laboratory

<sup>3</sup> University of Ioannina, Archaeometry Center

<sup>4</sup> National Technical University of Athens, Department of Applied Mathematic and Physical Science

## Abstract

A preliminary study has been performed estimating the residence time of a submarine groundwater discharge in Kalogria Bay (SW Peloponnissos, Greece). A number of naturally occurring radio-nuclides ( $^{222}\text{Rn}$ ,  $^{214}\text{Pb}$ ,  $^{214}\text{Bi}$ ,  $^{228}\text{Ac}$ ,  $^{208}\text{Tl}$ ,  $^{40}\text{K}$ ) have been used as tracers measuring samples of sea, rain and groundwater by means of LSC and HpGe. Radon daughters measurements were also performed using the *in situ* underwater autonomous gamma-ray detection system "KATERINA". The estimation of the residence time of groundwater has been attempted using a different approach to standard methods, based on activity ratio concentrations of radium daughters

*Keywords: Radionuclides, Instruments And Techniques, Monitoring, Brackish Water, Aegean Sea*

## Introduction

During the last decades, submarine groundwater discharge (SGD) has been recognized as an important hydrological mechanism affecting numerous phenomena (e.g. elements cycles, contamination by heavy metals and radionuclides, eutrophication) relating to the coastal zone. The main methods for detection and quantification of SGD are based on: a) direct physical measurements with e.g. seepage flux meters; and b) tracer techniques, estimating the concentrations of geochemical substances which are naturally enriched in groundwater paths. Amongst the tracer techniques, those based on radioactive isotopes as radium, radon and their daughters were used in several studies to investigate the temporal and spatial distribution of SGD [1, 2], the coastal mixing rates [3] and the residence time of groundwater through the aquifer paths [4]. In this work, a radiological study is presented involving numerous radiotracers ( $^{40}\text{K}$ ,  $^{222}\text{Rn}$ ,  $^{214}\text{Pb}$ ,  $^{214}\text{Bi}$ ,  $^{226}\text{Ra}$ ,  $^{228}\text{Ac}$ ,  $^{208}\text{Tl}$ ,  $^3\text{H}$ ) for the estimation of groundwater residence time of the SGD point source located in Kalogria Bay (SW Peloponnissos).

## The study area, materials and methods

The Kalogria Bay is located in southwestern Peloponnissos, in the Messinia prefecture. Many locations of submarine groundwater discharges are easily visible around the bay, although the main SGD point source is located ~180 m offshore. At this location, groundwater is emanating into the sea mainly through a small submarine cave at 25 m depth. The site is reached by small boats and divers are occupied to collect water samples and to deploy inside the cave a small lander equipped with several sensors. *In situ* measurements are performed by "KATERINA", an autonomous underwater gamma-ray NaI (Tl) detector [5, 6], monitoring the radioactivity concentration of radon daughters ( $^{214}\text{Pb}$ ,  $^{214}\text{Bi}$ ),  $^{228}\text{Ac}$ ,  $^{208}\text{Tl}$  and  $^{40}\text{K}$ . Also, for subsequent measurements in laboratory, a quantity of 10 mL from the water samples is immediately added by syringe inside plastic vials containing 10 mL of scintillation cocktail. The vials are transported to the laboratory within the first 24 hours after sampling, for gross alpha and beta counting of radon and its daughters by a Liquid Scintillation Counter (LSC) TriCarb 3170 TR/LS. Furthermore, 0.6 L of water samples are measured in the laboratory by means of a High Purity Germanium detector (HpGe) for any gamma-ray emitter. In addition, after a simple distillation procedure 8 mL of groundwater, water from terrestrial springs, and rain are added in glass vials containing 12 mL of scintillation cocktail for tritium ( $^3\text{H}$ ) concentration measurements by LSC method.

## Results and Discussion

*In situ* gamma-ray spectra from "KATERINA" detector exhibits radon daughters contributions since gamma-ray emitters at 351 keV ( $^{214}\text{Pb}$ ), 609 keV ( $^{214}\text{Bi}$ ) are clearly observed. Measured  $^{214}\text{Pb}$  and  $^{214}\text{Bi}$  activities are  $550 \pm 45 \text{ Bq/m}^3$  and  $575 \pm 45 \text{ Bq/m}^3$ , respectively. The activity of  $^{40}\text{K}$  is  $11300 \pm 95 \text{ Bq/m}^3$  while  $^{228}\text{Ac}$  and  $^{208}\text{Tl}$  exhibit activities of  $130 \pm 11 \text{ Bq/m}^3$  and  $160 \pm 15 \text{ Bq/m}^3$  respectively. Radon activity concentration by the LSC method during the same period (July 2009) exhibited values varying from  $1200 \pm 100$  to  $800 \pm 100 \text{ Bq/m}^3$ . Regarding  $^3\text{H}$  concentration, the estimated values varied between  $4.3 \pm 1.7$  to  $5.9 \pm 1.7 \text{ TU}$ . These measurements have to be combined with  $^3\text{H}$  measurements of rainwater collected from the same region in order to achieve an ageing of the water. Also, a method for the residence time

estimation of groundwater was applied, as proposed in the literature [4]. This model assumes the investigating system is in steady-state which means that radium isotopes additions (radium flux from groundwater) are balanced with losses (mixing and radioactive decay). The activity ratio of  $^{224}\text{Ra}/^{228}\text{Ra}$  has been substituted by  $^{208}\text{Tl}/^{228}\text{Ac}$  as  $^{228}\text{Ra}$  and  $^{228}\text{Ac}$  reach a secular radioactive equilibrium after 1.5 days while the activity ratio of  $^{224}\text{Ra}$  to  $^{208}\text{Tl}$  remains constant ( $\approx 2.6$ ) after 2 days. By means of a HpGe detector, radium daughter isotopes  $^{208}\text{Tl}$  ( $^{224}\text{Ra}$ ) and  $^{228}\text{Ac}$  ( $^{228}\text{Ra}$ ) concentration activity ratios was calculated into the groundwater path (outlet region), as well as in the inventory where the groundwater discharges. The residence time using the aforementioned model was calculated at  $2.5 \pm 1.3$  days. The increased uncertainty is due to low concentrations mainly of  $^{228}\text{Ra}$  daughter ( $^{228}\text{Ac}$ ). The sensitivity of the applied method for the estimation of the residence time would drastically be improved measuring in a lower gamma-ray background environment.

## Conclusions

During the period 2009-2010, a comprehensive study is in progress at the SGD site in Kalogria Bay (SW Peloponnissos). Radioactive tracer techniques are being applied estimating groundwater's residence time by means of HpGe gamma-ray spectrometry, and the water age by means of  $^3\text{H}$  concentration by LSC method. Also, the application of *in situ* gamma-ray spectrometry method based on "KATERINA" detector offers simultaneously concentrations of  $^{40}\text{K}$  (relative to salinity) and  $^{214}\text{Bi}$ ,  $^{214}\text{Pb}$  (relative to radon concentration), which are strongly correlated with the mixing processes between ground and sea water at the SGD site. These long term measurements will also contribute significantly to the estimation of water velocities and water flux rate of the specific SGD source.

## References

- 1 - Burnett W. C. and Dulaiova H., 2006. Radon as a tracer of submarine groundwater discharge into a boat basin in Donnalucata, Sicily. *Cont. Shelf. Res.* 26, 874-884.
- 2 - Burnett W. C., Peterson R., Moore W. S., and de Oliveira J., 2008. Radon and radium isotopes as tracers of submarine groundwater discharge - Results from the Ubatuba, Brazil SGD assessment intercomparison. *Estuarine, Coast. Shelf. Sci.* 76, 501-511.
- 3 - Moore, W.S., 2000. Determining coastal mixing rates using isotope radioisotopes. *Cont. Shelf. Res.* 20, 1993-2007.
- 4 - Moore, W.S., Blanton, J.O. and Joye, S.B., 2006. Estimates of flushing times, submarine groundwater discharge, and nutrient fluxes to Okatee Estuary, South Carolina. *J. Geophys. Res.* 111, C09006.
- 5 - Tsabaris, C., Bagatelas, C., Dakladas, Th., Papadopoulos, C.T., Vlastou, R., Chronis, G.T., 2008. An autonomous *in situ* detection system for radioactivity measurements in the marine environment. *App. Radiat. Iso.*, 66, 1419-1426.
- 6 - Tsabaris C., Scholten J., Karageorgis A.P., Commanducci J-F., Georgopoulos D., Kwong L-L.W. and Papathanassiou E., 2009. Application of an *in situ* underwater gamma spectrometer as a marine radon progeny monitor: continuous monitoring of groundwater discharges into the coastal zone. *J. Environ. Radioactiv.*, submitted