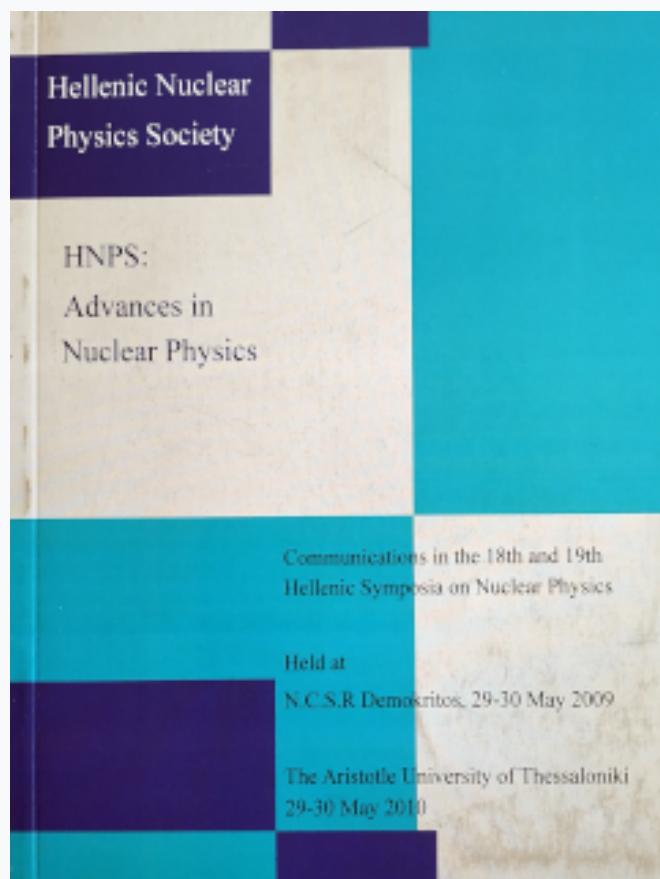


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Radio-tracing techniques applied in a marine ecosystem, the case of a submarine groundwater source at southern Peloponnesus.

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Abstract

The submarine discharge of groundwater (SGD) into the coastal zone has been recognized as an important component of the hydrological cycle. Quantities of groundwater flowing toward coastal aquifers are leaded under the seafloor and due to geomorphologic causes may discharge into the coastal zone. At some locations the quantity of the water is large enough to establish these springs as valuable water sources. The estimation of the submarine groundwater flux is complicated by conventional methods. Instead, measurements of a variety of radioisotopes (^{222}Rn , ^{214}Pb , ^{226}Ra , ^{228}Ra , ^{40}K , ^3H) as tracers provide a means to obtain integrated flux estimations as well as residence time, the age of the water and a factor of ground-sea water mixing process. Results from the current study at Stoupa's (S. Peloponnesus) SGD source are presented revealing the importance of radio-tracing methods to the investigation of marine ecosystems.

Key words: Marine ecosystems, submarine groundwater discharge, radio-tracing techniques.

1. Introduction

Groundwater contains enhanced radon concentrations, in comparison with surface or sea water, due to radium presence and decay in aquifers soil and rocks. There are four isotopes of radium in subsoil as partners of the primordial natural radioactive series of uranium and thorium but the most abundant is radium ^{226}Ra . Radon ^{222}Rn is the first decay product of ^{226}Ra and is an inert gas. It is transported into groundwater by diffusion through the aquifer soil or by the decay of diluted ^{226}Ra inside the groundwater mass. Despite the potential hazard for the public health which follows the use of enhanced radon groundwater, radon may be served as a radio-tracer in multiple hydrological studies. As noble gas does not react chemically with aquifer solids or other substances into the water, it is entirely dissolved, it has a short half life (3.8 days) and can be measured directly [1].

Radon has been already utilized as tracer in many studies around the world concerning mainly the subsurface discharge of groundwater from coastal aquifers into the sea, usually called SGD [2]. In general, this discharge contains meteoric water from land drainage and possibly seawater which may enter from coastal aquifers. A more detailed definition of SGD has been reported [3] while many studies consider the phenomenon as an important pathway of dissolved matter transport to the ocean [4-6]. There are three main sources of SGD: i) coastal freshwater aquifers where SGD is driven by the hydraulic gradient between land and sea; ii) re-circulated seawater in which tides and/or internal waves cause a circulation of seawater through coastal sediments; and iii) a mixture of both i) and ii).

The detection and quantification of such sources is realized by direct measurements with e.g. seepage flux meter or by tracer techniques. The later are based on measurements of geochemical species which are naturally enriched in SGD relative to seawater. As groundwater is rich of radon, many studies use this noble radioactive gas to quantify the emanating water and to investigate the temporal and spatial distribution of SGD [5], [7-8]. Measurements of radon are conducted either by laboratory based methods like, e.g., liquid scintillation [9], or by stripping of radon from a water sample [10] and consecutive measurement in the laboratory. Although these methods are well established, cannot provide extended time-series. When the temporal behaviour of a source and the fluctuations of radon concentration are needed, in-situ methods prevail in advantages as the detection systems are immersed exactly on the point of interest monitoring continuously for several days. However such applications are scarce due to the instrumentation which needed for detection purposes. They require special, fully-integrated detection systems able to withstand many hardships (e.g. enhanced pressure and mechanical stress, chemical corrosion fatigue etc.) due to “unfriendly” acquiring conditions.

The Hellenic Centre for Marine Research (HCMR) has developed an autonomous underwater gamma-ray spectrometer named “KATERINA” [11]. As this study is still in progress (May 2010) the article presents some first results from the deployments (July 2009 to December 2009) of the system into the submarine source of Stoupa. Also, the age of the groundwater has been estimated comparing the activity concentration of tritium ^{3}H in groundwater with rain water. Finally, as it is described with details elsewhere [12], it is possible to estimate the residence time of the flowing water into the groundwater paths using the activity concentration of radium isotopes.

2. Study area and experimental set up.

The SGD site at Stoupa, named after the small town of Stoupa in SW Peloponnesus, is located ~500 m off the coast. Limestones and dolomites, and to a lesser extent metamorphic rocks characterize the geological make-up of the coastal zone. The carbonate rocks are heavily karstified and almost completely permeable. The submarine springs have been first recorded in 1975, though local inhabitants are well-aware of their existence and claim that the springs have never stopped emanating water for at least the past 60 years. Although, the main spring discharges water from significant depth (~26 m), the strength of the outflow generates a gyre at the surface, which is clearly visible, particularly under calm weather conditions. Preliminary observations by scuba divers revealed a system of four locations of SGDs, two strong (in terms of discharge) ones and two smaller ones all

within a distance of less than 100 meters. The two strongest SGDs emanate directly from rocks, with very strong currents especially during winter.

Inside the main underwater spring, in a depth of 26m, a measuring station was immersed by a team of divers. Onto the station an underwater gamma-ray spectrometer was attached in combination with a passive aquatic listener (PAL), rotor flow meters and conductivity/temperature (CT) data loggers (see figure 1). The spectra were stored, after 12h of acquisition, in a special memory which is incorporated in the system and they were extracted after the recovery of the measuring station. The analysis of the spectra was performed with SPECTRW software. Radon progenies (^{214}Pb and ^{214}Bi) and potassium ^{40}K activity concentrations were quantitatively measured in Bq/m^3 using the appropriate marine efficiency parameters [13]. Also, a number of groundwater samples were collected by the divers. A small quantity (10ml) of groundwater, immediately after the collection, was ejected by syringes into plastic vials containing liquid scintillator. These samples were transported within 24h to the Archaeometry centre of University of Ioannina and were counted by means of a liquid scintillation counter (LSC) providing the activity concentration of radon ^{222}Rn itself. Moreover, to obtain the activity concentration of tritium ^{3}H , 100 ml of groundwater after standard preparation procedures (filtration, evaporation) were also measured by the LSC method.

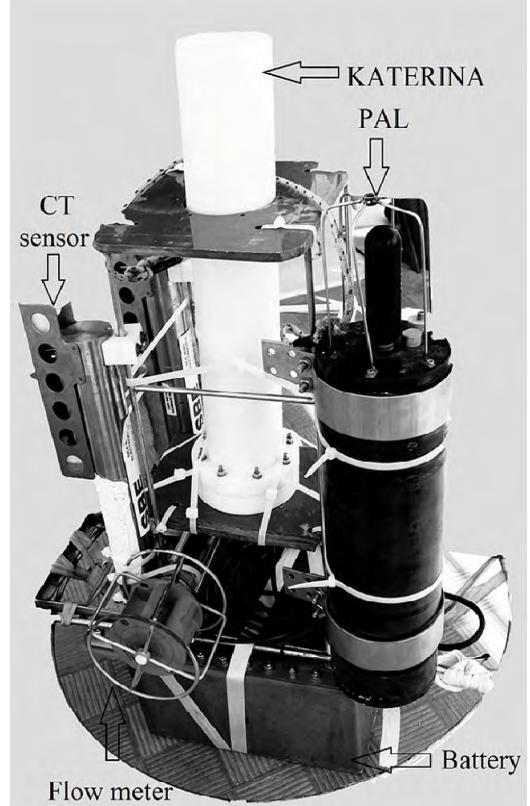


Figure 1. The station with several sensors including the underwater gamma-ray spectrometer KATERINA

3. Results and discussion.

3.1. Radon progenies and potassium time-series.

From the autumn to winter of 2009, a number of deployments of the measuring station took place, during a meteorological period with wet (rainfalls) and dry (no rainfalls) terms. Significant variations in the flow rate of the SGD were observed, which were reflected in the flux velocity measurements. In figure 2 indicative data concerning flux velocity and activity concentrations are plotted as time-series. During October and November of 2009 the activity concentration of radon progenies (^{214}Pb and ^{214}Bi) exhibits a strong correlation with flux velocity (flow rate). Although ^{214}Bi data are presented, ^{214}Pb was found in radioactive equilibrium with ^{214}Bi , and thus ^{214}Pb exhibits the same behaviour. In contrast, the activity concentration of ^{40}K was found inversely proportional to flux velocity. The above results have a physical interpretation. The emanating water may contain radon enhanced groundwater and seawater

which is rich in potassium and almost radon free. During the wet periods the amount of the groundwater into the emanating water is increased (against the re-circulated seawater), resulting greater flow rate/velocity and radon concentration. Conversely, during dry terms the amount of the groundwater is decreased causing lower levels of radon progenies activity concentrations and higher

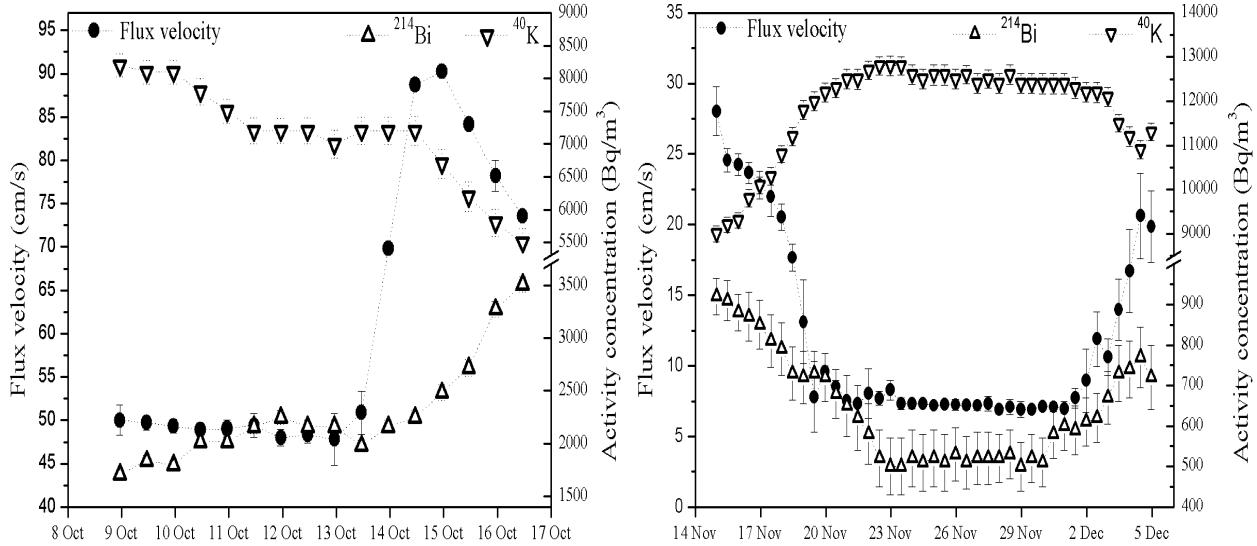


Figure 2: The activity concentration of radon progeny ^{214}Bi and potassium ^{40}K as time-series in respect with the velocity of the emanating groundwater. The radon progeny of ^{214}Pb was found in radioactive equilibrium with ^{214}Bi

levels of potassium. Also, till the current stage of the study, the radon measurements by LSC methods revealed no equilibrium between radon and its progenies. For instance, during the first deployment (late of July 2009) the activity concentration of radon was measured (by LSC) two times greater than its progenies (measured by KATERINA). As the water flows continuously, the time that a quantity of water remains in the vicinity (effective volume) of the underwater detector is not sufficient for a state of secular equilibrium between radon and its progenies to be reached.

3.2. Groundwater ageing using tritium concentrations.

Tritium is produced in the upper layers of the atmosphere from the interaction of cosmic rays (fast neutrons) with atmospheric nitrogen. It can combine with oxygen to form tritiated water (really heavy water) and following the water circle enters into the sub-soil aquifers from precipitation. Its half-life of 12.32y makes it an important tool to hydrology as age dating radio-tracer. In this study, the average value of activity concentration of tritium (in tritium units) containing in the groundwater of two submarine springs (SGD1 and SGD2) was compared with those into rainwater and terrestrial groundwater (Terr.1-5). As the study is still in progress, the so far results are depicted in figure 3. The main observation is the slight differences (less than the statistic error) of the measured activities of tritium from the sources in comparison with the levels of tritium in the rainwater (dot-line fig.3).

This fact is a strong indication of the small age of the groundwater which means that it remains into the aquifer for a short time period (less than six months according to detection limit) before emanates from a submarine or a terrestrial source. For accurate estimation of the groundwater age, pre-concentration of tritium from more massive samples via electrolysis has to be followed. Although the outcome was not estimated accurately, the fact that the age of the water does not outgo a period of approximately six months, may be turn into significant information for hydrologists.

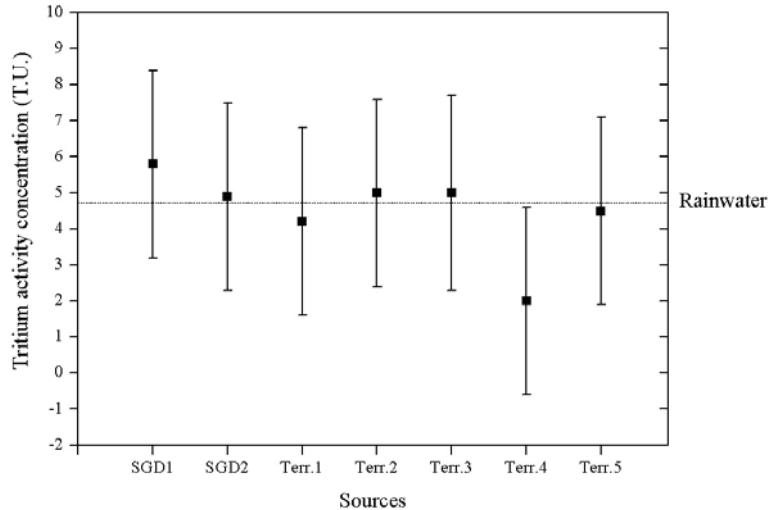


Figure 3. Activity concentration measurements (mean values) of tritium in groundwater emanating from submarine and terrestrial sources in comparison with the average tritium level of rain.

4. Conclusions

In this study was attempted the use of radio-tracing techniques in the investigation of a submarine groundwater source located near shore from Stoupa village / southern Peloponnesus. The underwater gamma-ray spectrometer KATERINA was utilized to record radon progenies (^{214}Pb and ^{214}Bi) and potassium (^{40}K) activity concentrations for long time periods providing results as time series. During the deployments of the winter of 2009, radon progenies activity concentrations revealed proportional fluctuations with the groundwater flux while potassium inversely proportional fluctuations. This fact indicates that an alternative method for flow rate estimations based on these radioisotopes could be developed. Also, using measurements of radon itself by means of a liquid scintillation counter, a non equilibrium state between radon and its progenies was revealed due to the fast moving of the water in the effective volume of the underwater spectrometer. The age of the ground water was estimated less than six months by the difference of tritium activity concentration in the groundwater and in the rainwater. Summarizing, in this study several radio-tracing techniques were used in combination with direct measurements of groundwater parameters (salinity, water flux, temperature etc). The so far results are promising for the development of new methods based on radioisotopes boosting the research of marine environment.

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