In situ underwater gamma-ray spectrometry as a tool to study groundwater–seawater interactions

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Abstract A new technology based on *in situ* underwater gamma-ray spectrometry of radon daughter products in water has been applied for groundwater–seawater interaction studies in the coastal regions of SE Sicily (offshore Donnalucata) and SE Brazil (offshore Ubatuba). The continuous monitoring carried out at the Donnalucata (and Ubatuba) site have revealed an inverse correlation between the ^{222}Rn concentration *versus* the tides and salinity, as ^{222}Rn concentrations in seawater varied from 2 kBq m^{-3} (1 kBq m^{-3}) during high tide to 5 kBq m^{-3} (5 kBq m^{-3}) during low tide. The observed variations in ^{222}Rn concentrations are likely caused by sea level changes, as tidal effects induce variations of hydraulic gradient, which can increase ^{222}Rn concentrations during a falling tide, while during a high tide, ^{222}Rn concentrations decrease.

Key words groundwater–seawater interaction; radon; radon decay products; seawater; submarine groundwater discharge; underwater gamma-spectrometry; SE Brazil; SE Sicily

INTRODUCTION

One of the frequently studied coastal processes is groundwater–seawater interaction (GSI) because of its importance for the protection of coastal zones against contamination from land-based sources, as well as for the management of freshwater resources in coastal areas (Burnett *et al*., 2006). Several isotope techniques for GSI studies have been developed using stable (^{2}H, ^{18}O, $^{87/86}$Sr, etc.) and radioactive (^{3}H, ^{14}C, Ra isotopes, ^{222}Rn, etc.) isotopes (Burnett *et al*., 2006; Povinec *et al*., 2006a). New technologies developed in recent years are based on analysis of radon or its daughter products emitting alpha-rays (Burnett *et al*., 2001; Burnett & Dulaiova, 2003, 2006; de Oliveira *et al*., 2003), or gamma-rays (Povinec *et al*., 2001; Levy-Palomo *et al*., 2004; Povinec, 2004, 2005; Povinec *et al*., 2006b,c).

Radon is a conservative radioactive tracer and because its concentration in groundwater is much higher than in seawater, it is an ideal tracer for studying GSI. ^{222}Rn is a decay product of ^{226}Ra (half life = 1.6 ky) in the ^{238}U natural decay chain and its short half life (3.82 d) makes it a suitable tracer for studying dynamic coastal systems. ^{222}Rn daughters are short lived radionuclides such as ^{214}Pb, ^{214}Bi, etc., which further decay by alpha and beta decays to ^{210}Pb (22.2 y) and ^{210}Po (138 d), and finally to stable ^{206}Pb. In the ^{232}Th decay chain there is another radon isotope, ^{220}Rn (thoron), with a very short half life (55.6 s). While ^{228}Ra (^{228}Ac) has been (as a part of the radium quartet, together with ^{226}Ra, ^{223}Ra and ^{224}Ra) used very often as a tracer of coastal processes (Moore, 2006), ^{220}Rn is still waiting for its applications in oceanography. Especially in coastal areas rich in thorium rocks, such as observed along the south-eastern Brazilian coast, ^{220}Rn may be a useful tracer of rapid coastal processes.

A coordinated research project (CRP) on "Nuclear and Isotopic Techniques for the Characterization of Submarine Groundwater Discharge (SGD) in Coastal Zones" has been jointly organized by the IAEA's Marine Environment Laboratories (IAEA-MEL, Monaco) and the Isotope Hydrology Section (Vienna), with the aim to develop new isotope techniques for studying SGD. The CRP has been carried out in cooperation with UNESCO's Intergovernmental Oceanographic Commission (IOC), the International Hydrological Programme (IHP), and several laboratories (Povinec *et al*., 2006a). In the framework of the CRP, two expeditions were carried out to the Ionian Sea (offshore Sicily), and one to offshore Ubatuba (Sao Paulo region, Brazil). It has been a great challenge to investigate SGD using underwater gamma-ray spectrometry in such different geological and hydrological environments.

METHODS

An underwater gamma-ray spectrometer (consisting of a 5 cm diameter and 15 cm long NaI(Tl) scintillation detector) previously developed for seabed mapping and stationary monitoring of radionuclides in seawater (Osvath & Povinec, 2001) was used in the GSI studies. Additional sensors for monitoring of temperature, water depth and wave impacts were located in front of the NaI(Tl) detector. The detector unit was connected via a 70 m long, double armoured steel coaxial cable to a PC with processing electronics and a multichannel analyser. The PC and an auxiliary low voltage power supply were located on a ship, or in a car when operating close to the coast.

The corresponding ^{214}Bi peaks (representing a decay product of ^{222}Rn) used in spectra evaluations were either at 609, 1120 or 1765 keV, depending on background conditions. The data acquisition system evaluates gamma-ray spectra every minute. Later, the obtained spectra are integrated to one hour intervals and the activity concentration of ^{214}Bi (and ^{222}Rn after calibration) in seawater is calculated. The system is fully automatic and can operate without any surveillance. The mean input flux of ^{222}Rn from ^{226}Ra present in sediments was estimated from measurement of ^{226}Ra activities of sediment samples. A detail description of the system and its calibration can be found in the papers of Povinec *et al*. (2006a,b).

RESULTS AND DISCUSSION

Study area offshore SE Sicily

In situ underwater gamma-ray spectrometry measurements were carried out from 16 to 25 March 2002 in the Donnalucata boat basin, where several sites, situated close to manual and automatic seepage meter posts, were occupied (Povinec *et al*., 2006b). Seepage rates of up to ~30 cm day^{-1} were reported by Taniguchi *et al*. (2006).

Time series of ^{222}Rn in seawater, salinity and tide were recorded at a site close to the coast. Results presented in Fig. 1 document that after the maximum tide the ^{222}Rn activity concentration of seawater was at minimum (down to 2.3 kBq m^{-3}), and after

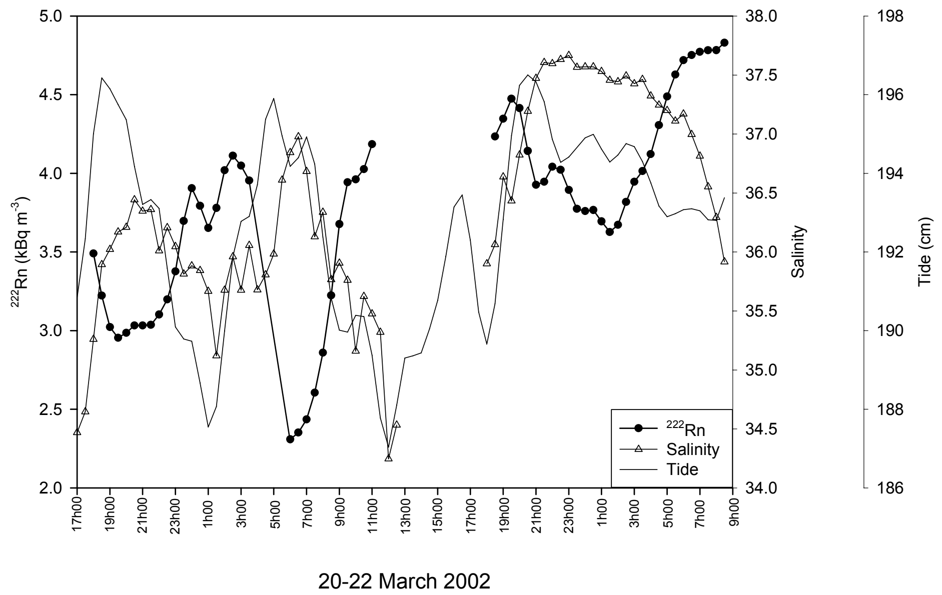

Fig. 1 Time series of radon concentration in seawater in the Donnalucata boat basin (Sicily) *vs* salinity and tide.

the minimum tide the ^{222}Rn activity concentration was at maximum (up to 4.8 kBq m^{-3}) with a delay of about one hour. A shift of approximately two hours was observed between the maximum tide and the salinity maximum.

Study area offshore SE Brazil

Time series of ^{222}Rn activity concentration in seawater, salinity and tide recorded from 22 to 26 November 2003 in Flamengo Bay (Ubatuba area) are shown in Fig. 2. The ^{222}Rn activity concentration in seawater varied between 1.0 and 5.2 kBq m^{-3}, while the tide varied between 4.4 and 5.6 m. The usual inverse relationship between the ^{222}Rn concentration in seawater and tide/salinity was not observed during 22 November, despite large variations in water levels. The observed changes in salinity during this time were, however, also smaller than during 25 and 26 November. The inverse relationship between the ^{222}Rn activity concentration in seawater and tide/salinity was, however, established from 23 to 25 November, when a few hours shift between the tide minimum/maximum and the ^{222}Rn maximum/minimum activity concentration was again observed.

Comparison of Sicilian and Brazilian results

In contrast to the Sicililian sites, which represent classic karstic terrain with low background radioactivity (^{238}U ~10 Bq kg^{-1} and ^{232}Th ~5 Bq kg^{-1}), the Brazilian site is in a tropical coastal area characterised by granite rocks where the concentrations of ^{238}U and ^{232}Th in the rock samples were higher by a factor of 5 and 10, respectively.

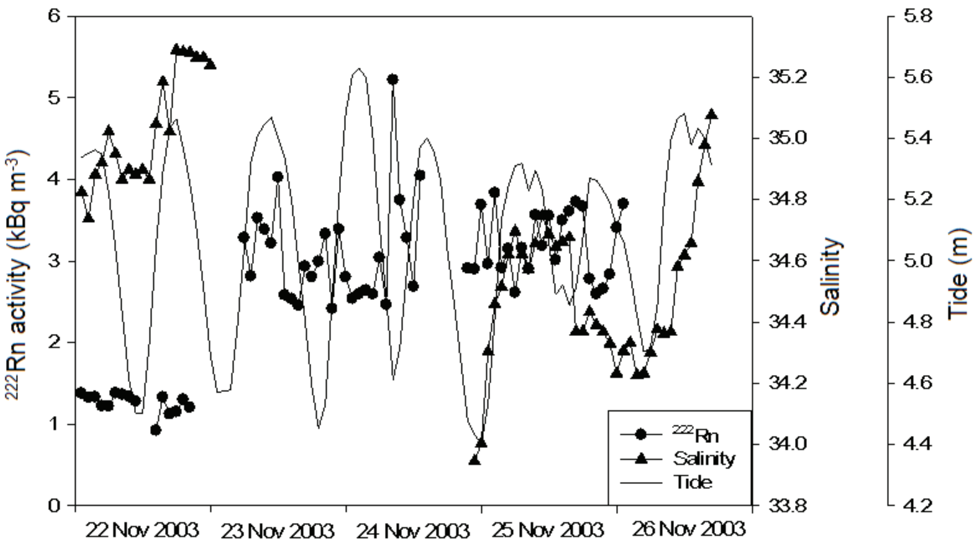

Fig. 2 Time series of radon concentration in seawater in Flamengo Bay (Brazil) *vs* salinity and tide.

The results obtained for Sicilian and Brazilian waters confirm the inverse relationship between tide and the ^{222}Rn concentration. During a falling tide, the observed ^{222}Rn concentration increases, while during a high tide the ^{222}Rn concentration decreases. While the ^{222}Rn concentration in Sicilian waters followed the tide with a delay of only one hour, in Brazilian waters a delay of several hours was observed. This is likely caused by the different oceanographic and hydrogeological conditions at both sites. The Sicilian coast is characterised by carbonate rocks with cracks, which facilitate groundwater transport to the sea, while along the Brazilian coast, granite rocks have lower transport capabilities. In spite of different geological/ hydrological settings, the ^{222}Rn activity concentrations in seawater at Sicilian and Brazilian sites were very similar, between 2.3 and 4.8 kBq^{-3}, and 1.0 and 5.2 kBq m^{-3}, respectively. Due to a factor of 5 higher ^{238}U concentration measured in granite than in carbonate rocks, higher ^{222}Rn activity concentrations along the Brazilian coast could have been expected. However, in Flamengo Bay, similar to that observed in the Donnalucata boat basin, the SGD may be represented by a mixture of re-circulated groundwater and seawater, having a lower ^{222}Rn concentration.

The inverse relationship between the ^{222}Rn activity concentration and tide in the Donnalucata boat basin was also reported by Burnett & Dulaiova (2006), who analysed ^{222}Rn by alpha-ray spectrometry of its daughter products. The temporal changes in ^{222}Rn concentration measured on 22 March 2002 (at a different point in the Donnalucata boat basin) were from 1.6 to 3.0 kBq m^{-3}, comparable with results presented in Fig. 1. They showed that the observed variations in ^{222}Rn activity concentrations can be related to SGD fluxes, and thus can be used for characterisation of SGD.

CONCLUSIONS

In situ underwater gamma-ray spectrometry measurements carried out during two expeditions in coastal waters offshore SE Sicily and SE Brazil showed the ability of the method to monitor SGD and to study its temporal and spatial variations. This new method of SGD investigations represents a robust technique that can be applied for long-term, continuous monitoring of radon in seawater and/or groundwater.

Time series measurements of ^{222}Rn activity concentrations generally confirmed an inverse correlation between the ^{222}Rn activity concentration and tide/salinity, caused by sea level variations as tide effects induce variations of hydraulic gradients, which increase ^{222}Rn concentrations during decreasing sea level, and opposite, during high tides ^{222}Rn activity concentrations are decreasing.

Such large changes in SGD, observed in a relatively small area, document again why the isotopic characterisation of SGD is important for estimation of real groundwater fluxes to the sea.

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